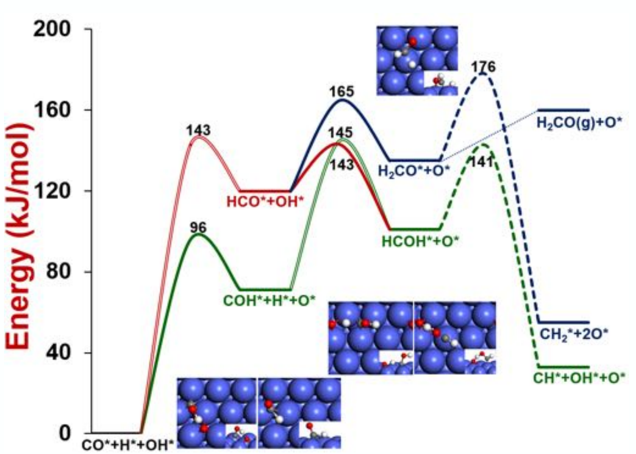
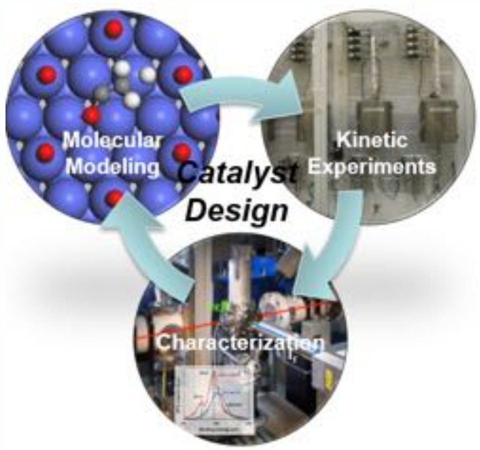
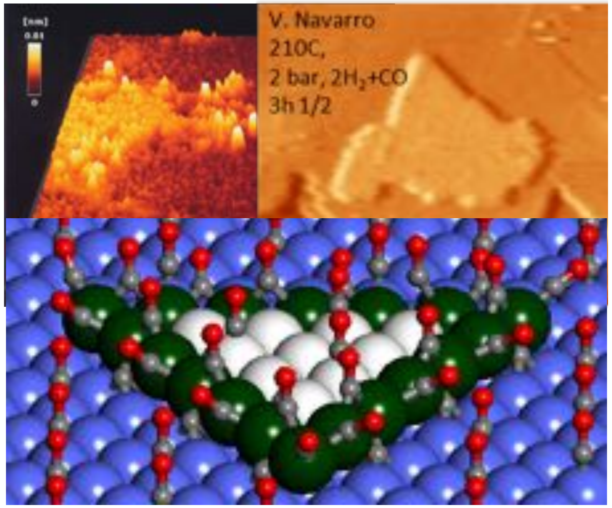
UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Catalyst structure and C-O activation during FTS: new ideas from computational catalysis







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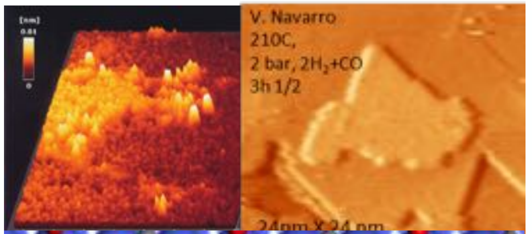
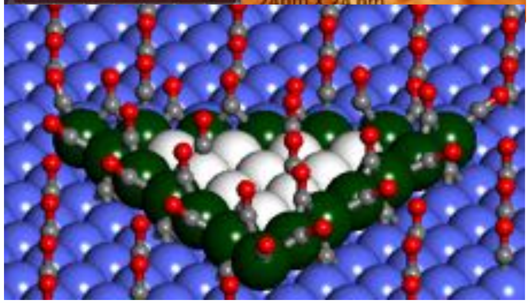
Outline





Structure: Reconstruction

Nature of experimentally observed islands

Origin of stability/formation

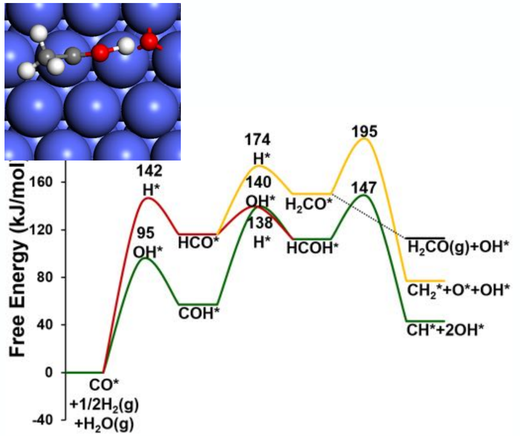
Refs: Banerjee *et al.*, *ACS. Catal.* **2015,** Banerjee *et al.*, **2016**

Activity: CO insertion and role of OH

CO insertion consistent with kinetic data

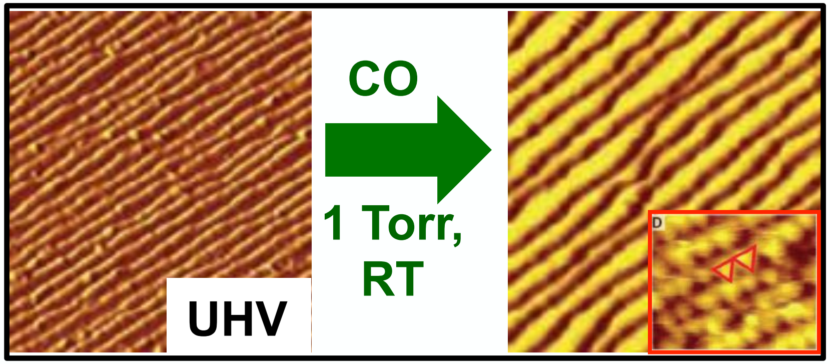
OH as hydrogenating species

Refs: Zhuo *et al.*, *JPCC* **2009**, Zhou *et al.*, *J. Catal.* **2013**, Gunasooriya *et al.*, *Surf. Sci.* **2015,** Gunasooriya *et al.*, **2016**

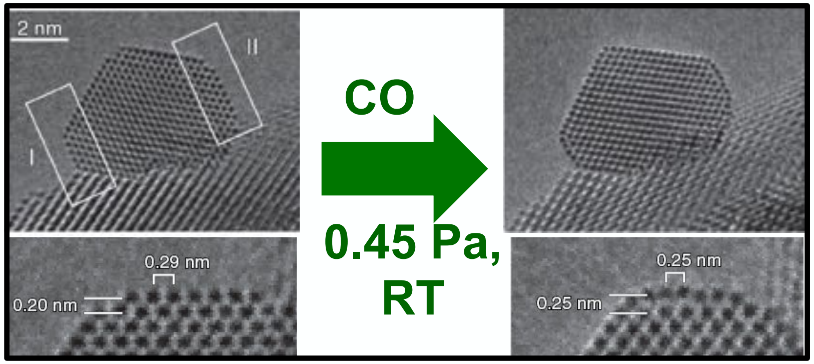


Surface reconstructions

Pt restructuring



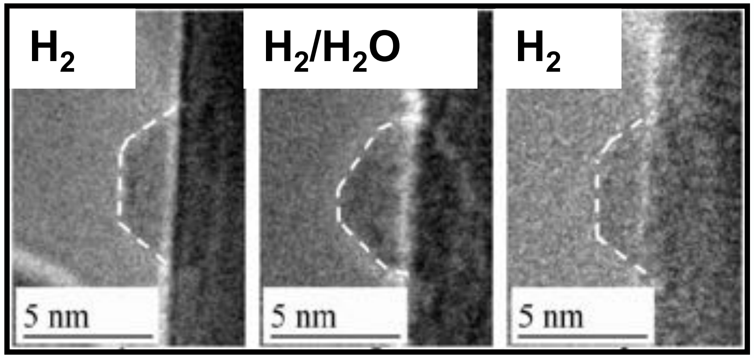
Au restructuring



- **Pt terraces form triangular nano-islands under CO**
  Ref: Somorjai *et al.*, *Science*, **2010**

- **Au nanoparticles restructure driven by stronger adsorption on reconstructed surface**
  Ref: Yoshida *et al.*, *Science*, **2012**

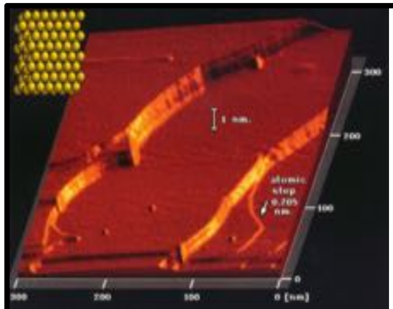
Cu restructuring



- **Cu catalysts restructure reversibly under H_2/H_2O at 1.5 mbar**
  Ref: Hansen *et al.*, *Science*, **2002**

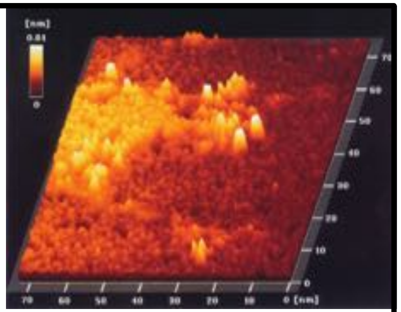
Massive reconstruction under FT conditions

STM images of effect of syngas on Co(0001)



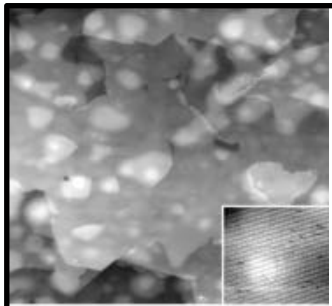
CO/H_2

4 bar, 523 K



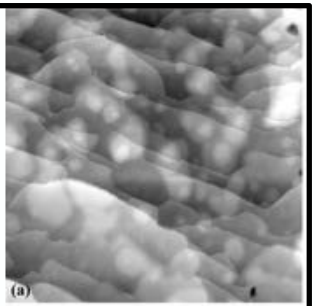
Islands

Ref: Wilson, de Groot, *J Phys Chem*, **1995**



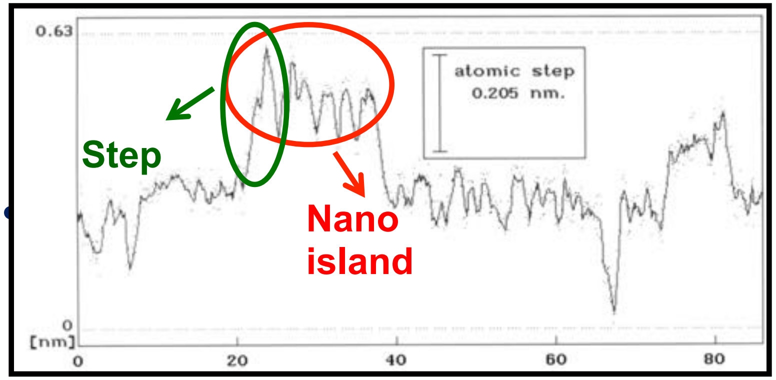
CO/H_2

10 mbar, 493 K



No Islands

Ref: Ehrensperger, Wintterlin, *J Catal*, **2014**



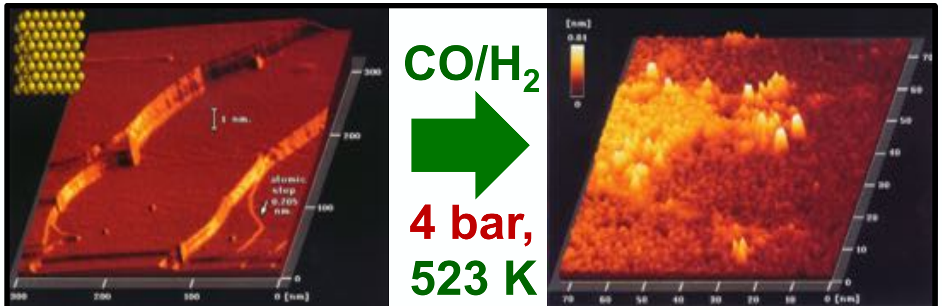
Massive surface reconstruction at FT pressures

Triangular nano-islands (~2 nm diameter)

What drives the formation of those islands?

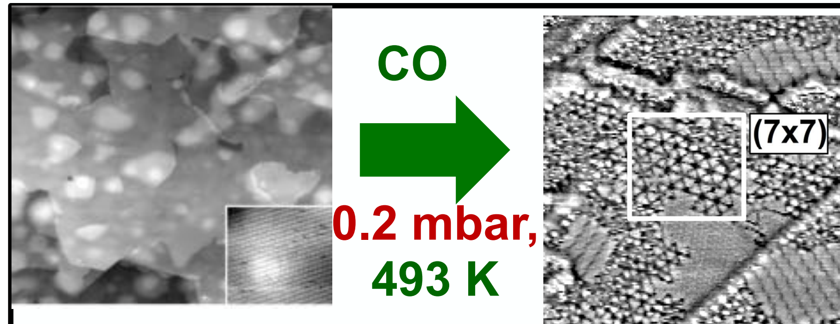
Massive reconstruction under FT conditions

STM images of effect of syngas on Co(0001)



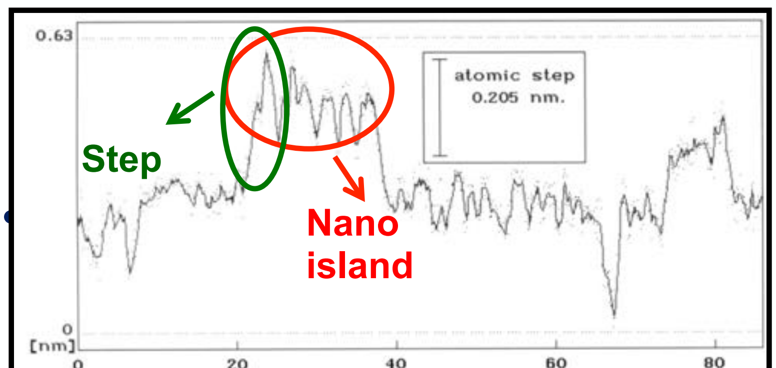
Islands

Ref: Wilson, de Groot, *J Phys Chem,* **1995**



Reconstruction

Ref: Wintterlin et al., *ACS Cat*, **2015**



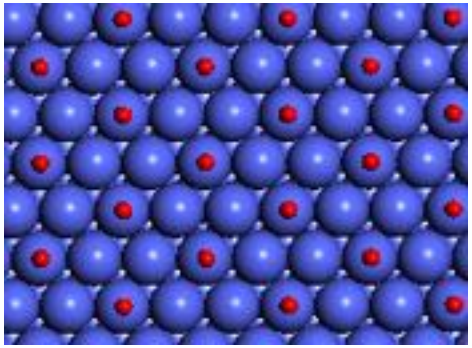
Massive surface reconstruction at FT pressures

Triangular nano-islands (~2 nm diameter)

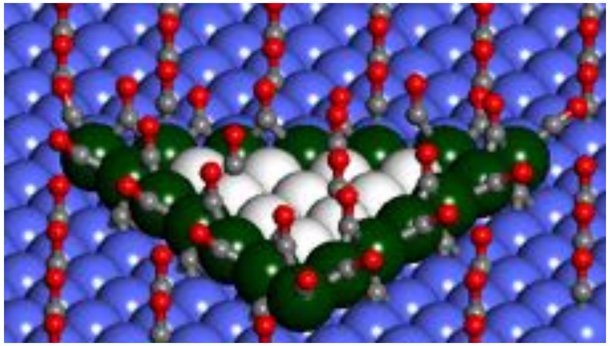
What drives the formation of those islands?

Structure of Co islands

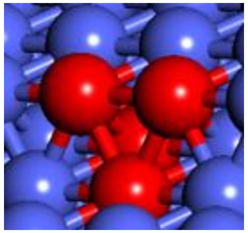
Island formation under reaction conditions



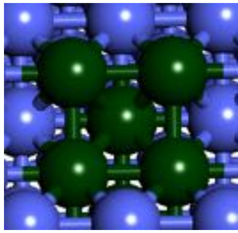
CO-covered terraces



Covered islands

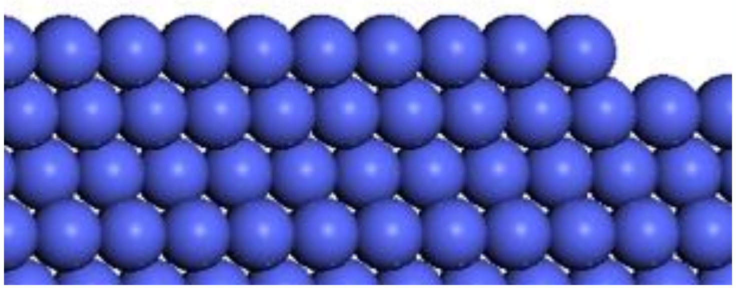


F4 site

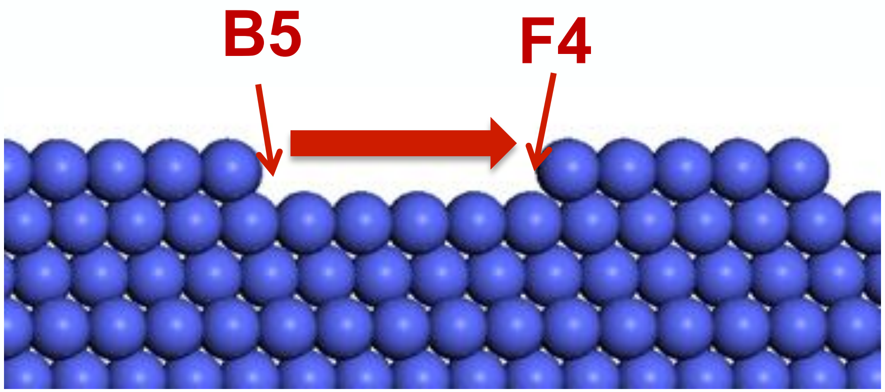


B5 site

Step creation



Clean Terraces

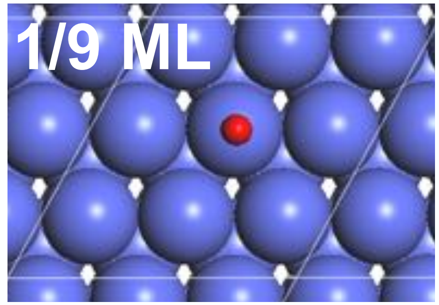


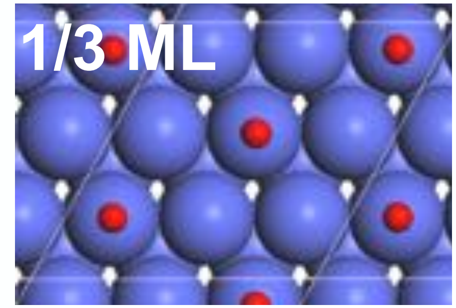
Formation of a step

Step creation: +85 kJ/mol step atoms (both sides)

Can we find adsorption combinations to overcome this penalty?

CO adsorption on Co and Pt





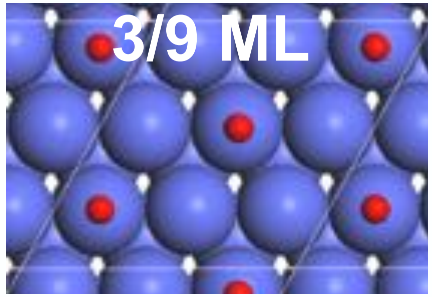
	Pt-1/9	Co-1/9	Pt-1/3	Co-1/3
VdW-DF	-143	-130	-139	-135
Experimental	-142	-128		

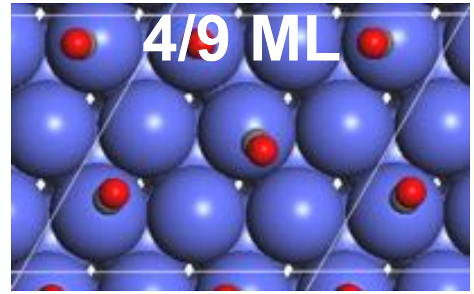
VdW-DF – accurate adsorption enthalpies

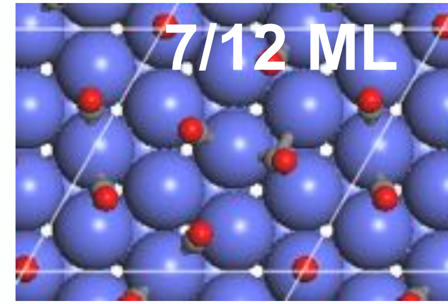
1/9 ML → 1/3 ML – attraction on Co, repulsion on Pt

Attraction → CO island formation (note: mixing entropy)

CO coverage on terraces? Phase transition







Differential E_{ads}	-135	-46	-75
ΔG_{ads}(500 K, 7 bar)	-65	+32	+6

Adsorption entropy: -140 to -150 J/mol K

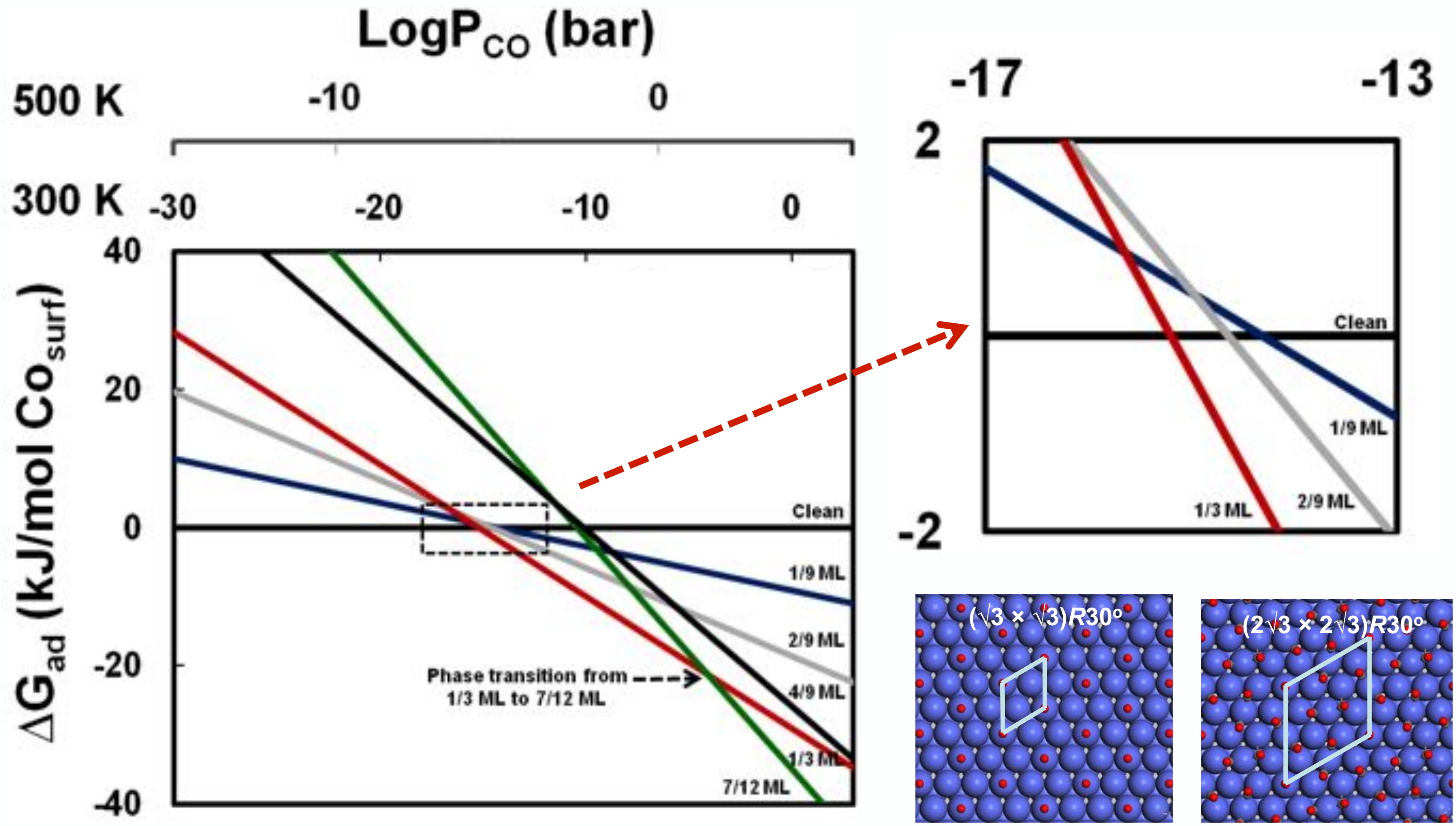
Stability: $\Delta G_{ads}(T, p) = \Delta H_{ads}^0(T) + T\Delta S_{ads}(T) + RT \ln(p/p_0)$

Differential E_{ads}: Co-1/3 ML CO + CO(g) → Co-x ML-CO

Co terraces saturated at 1/3 ML (500 K, 7 bar CO)

Phase transition to 7/12 ML, not gradual increase

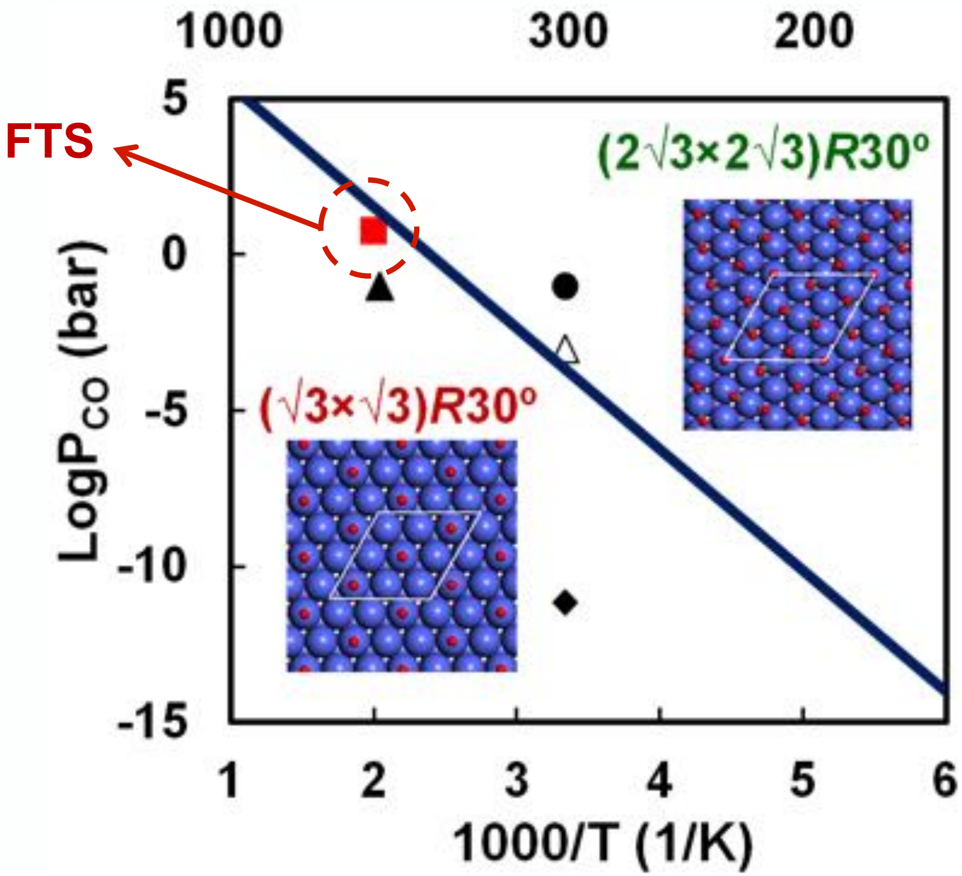
CO coverage on terraces? Phases



Low pressures: isolated ($\sqrt{3}\times\sqrt{3}$)R30°-CO islands

Higher pressures: phase transition to ($2\sqrt{3}\times2\sqrt{3}$)R30°-7CO phase

Phase diagram CO on Co terraces



Two phases on Co terraces, separated by a first-order phase transition

Calculations reproduce exp. phase transitions

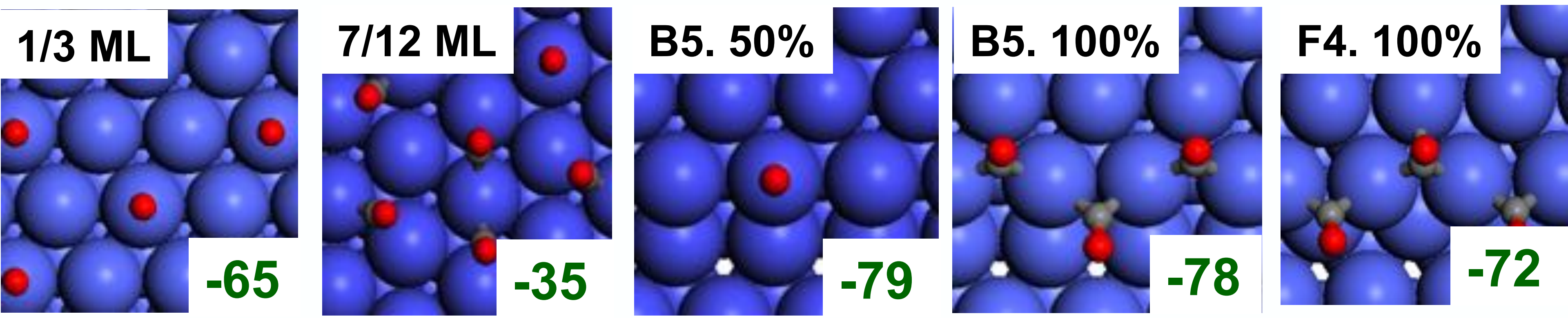
Coverage under FT: 1/3 ML or 7/12 ML

Zhou, Borgna, Saeys, J. Catal., **2013**; Saeys et al, Surf. Sci. **2015; Exp:** Bridge et al., Surf. Sci. **1977**; Beitel et al., JPC B **1997**

CO adsorption at step edges

First principle CO adsorption free energy (~T, p, composition)

$$\Delta G_{ads}(T, p_{CO}) = \Delta H_{ads}(T,p_{CO}) - T\Delta S_{ads}(T, p_{CO}) + RT\ \ln(1/p_{CO})$$



ΔG_{rxn} to create step:

Desorption of CO (3 rows*1/3 ML*65 kJ/mol) + Step creation (85 kJ/mol)
- CO adsorption at B5 and F4 (100%*78 kJ/mol +100%* 72 kJ/mol)

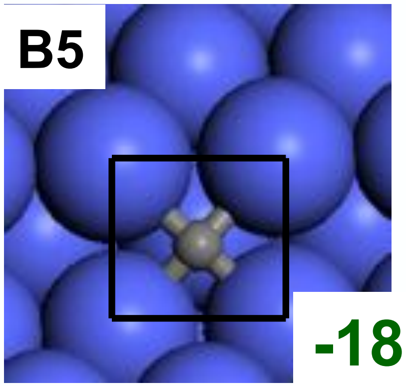
~ 0 kJ/mol steps

Stronger CO adsorption and high CO coverage overcome step-creation energy under FT conditions

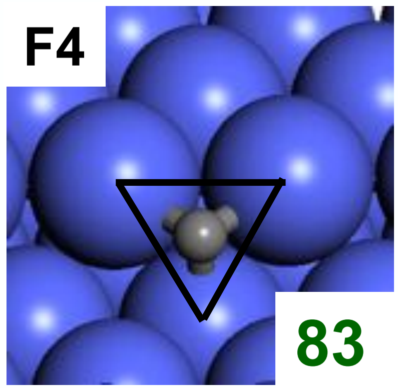
Can we increase driving force?

Strong square-planar carbon adsorption

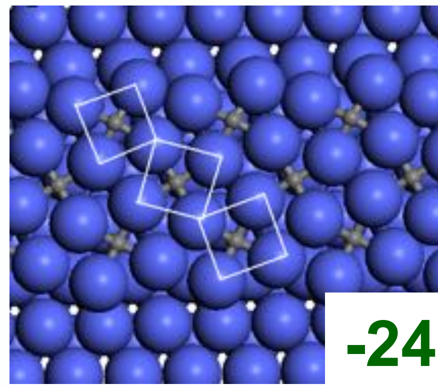
Carbon stability: ΔG_{rxn} for $CO(g) + H_2(g) \rightarrow [C]^* + H_2O(g)$



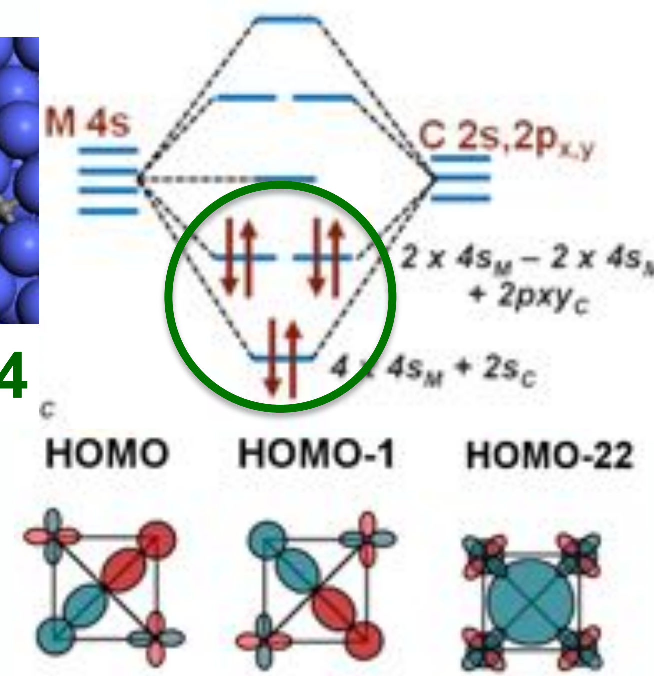
Carbon at B5 steps



Carbon at F4 steps



Surface carbide on islands



4n+2 Huckel rule
-> σ-aromaticity

Under FT conditions, square-planar carbon binds strongly at B5 site

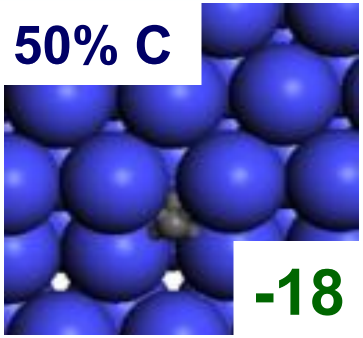
Unique stability (cf. graphite: -69 kJ/mol) due to σ-aromaticity

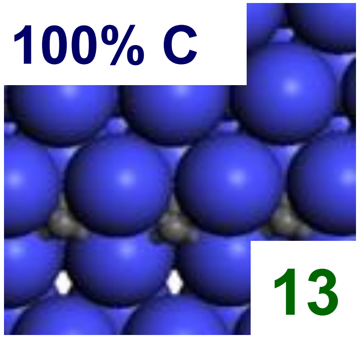
Ciobica *et al.* **2008,** Tan, Xu, Chang, Borgna, Saeys, *J. Catal.*, **2010**
Nandula, Thang, Saeys, Alexandrova, *Angew. Chem.*, **2015**

C/CO coverage at B5 steps?

Carbon stability:

ΔG_{rxn} for $CO(g) + H_2(g) \rightarrow [C]^* + H_2O(g)$



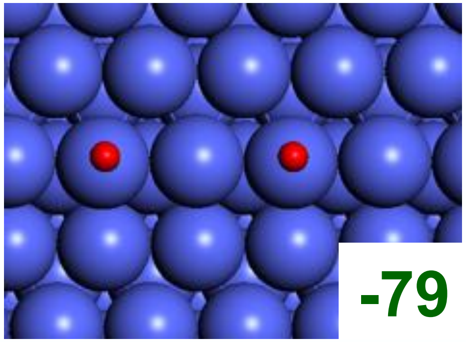


C coverage beyond 50% not favorable due to electron count and σ-aromaticity

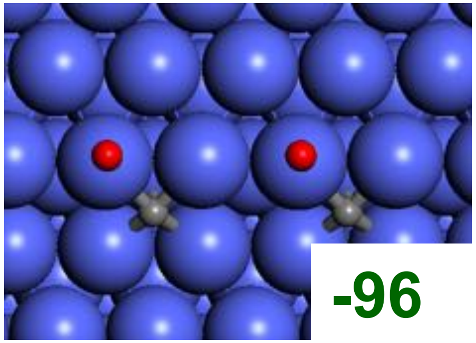
Sites available for reaction?

CO stability:

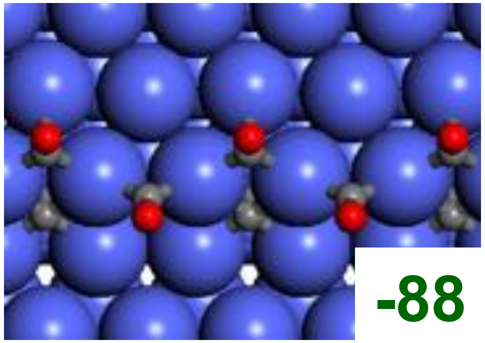
B5 50%



50% C + 50% CO

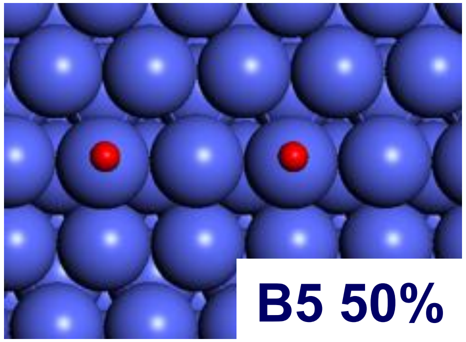


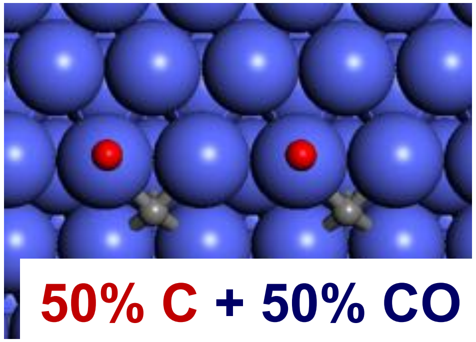
50% C + 100% CO

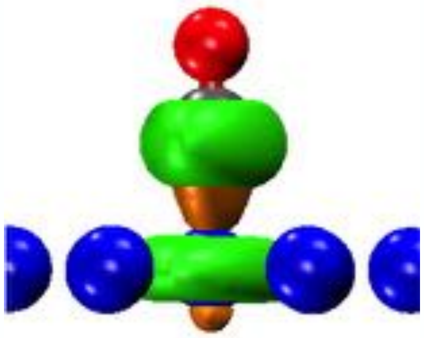


Square planar C increases CO stability

C increases CO adsorption. NBO analysis







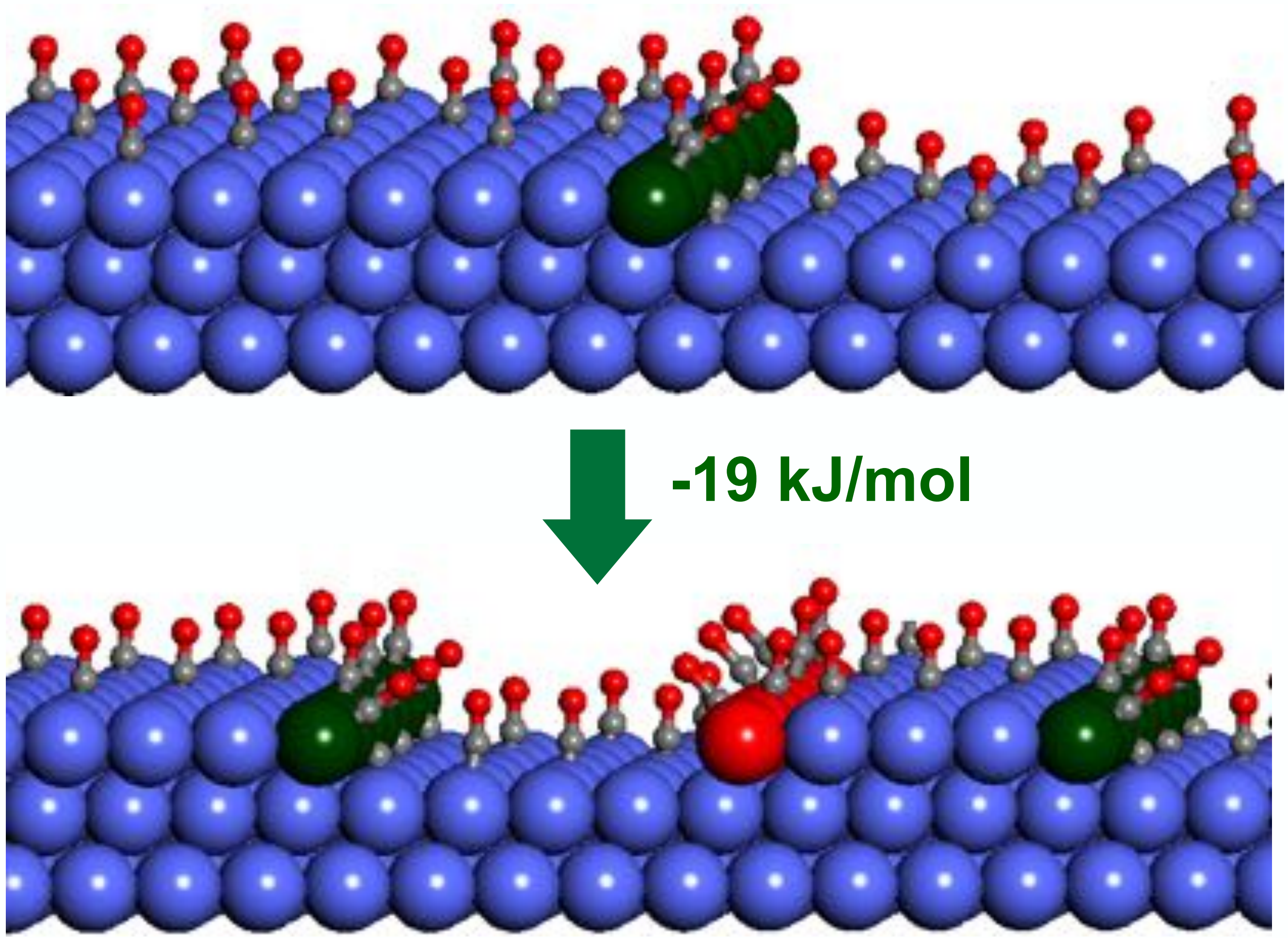
	B5	B5+50%C
ΔG_{ads} (kJ/mol)	-79	-96
(Co-C)* NBO	0.36	0.33
Co charge	-0.1 e	-0.4 e
Co 2p XPS (eV)	778.1	779.6

Reduced Co–CO Pauli repulsion due to carbon

Square-planar C oxidizes Co -> experimental fingerprint

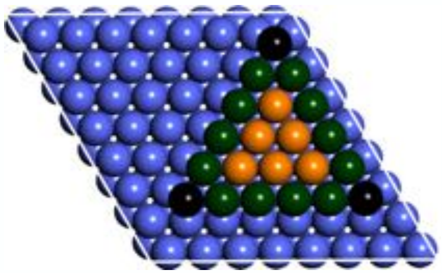
Periodic NBO method: Schmidt et al., *JCTC*, **2012**

Stability of C/CO covered B5 steps

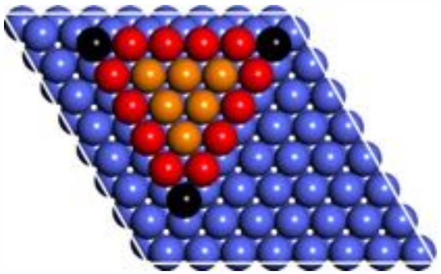


50% C and 100% CO step edge coverage overcomes energy penalty to create steps and stabilizes B5

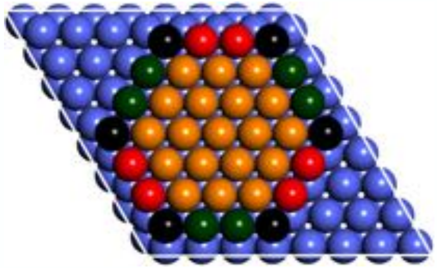
Fomation of islands – Shape and size



B5 island

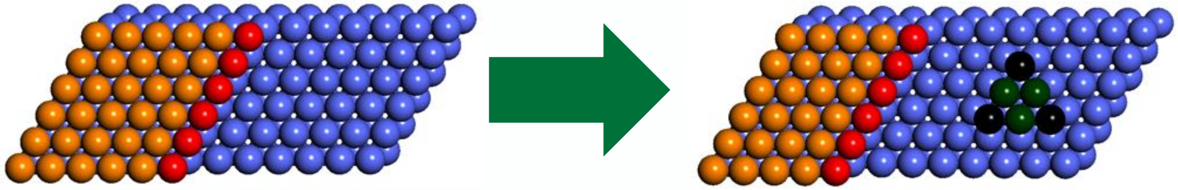


F4 island

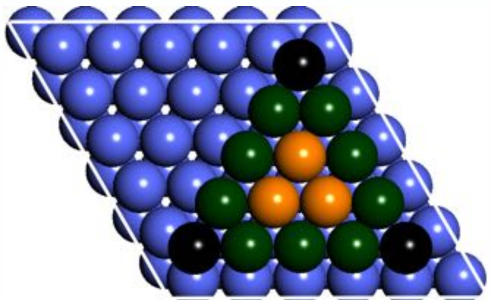


Hexagonal island

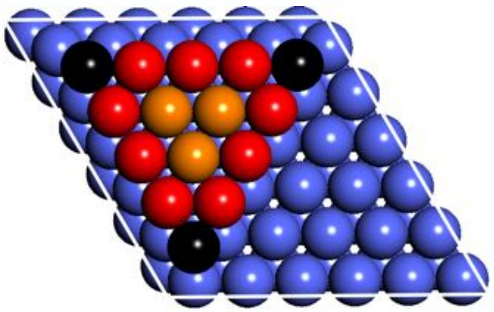
How do islands form?



Estimation of island creation energy - Example



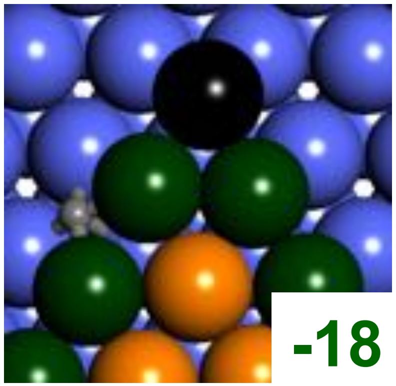
472 kJ/mol



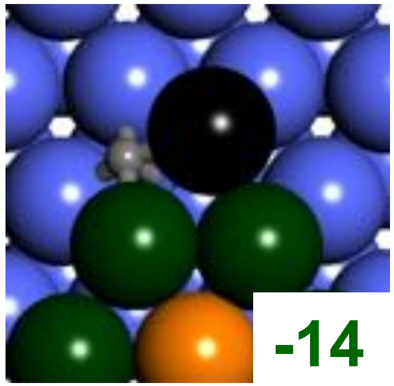
421 kJ/mol

C/CO adsorption at corners

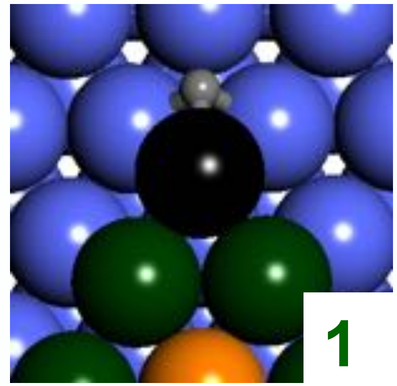
Carbon stability: ΔG_{rxn} for $CO(g) + H_2(g) \rightarrow [C]^* + H_2O(g)$



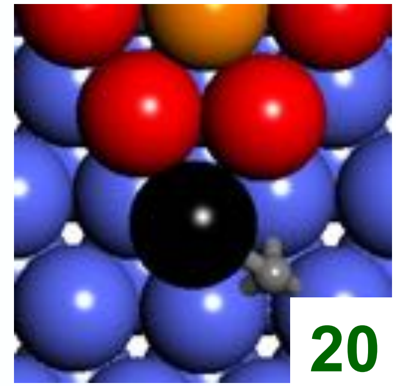
B5



B5_corner

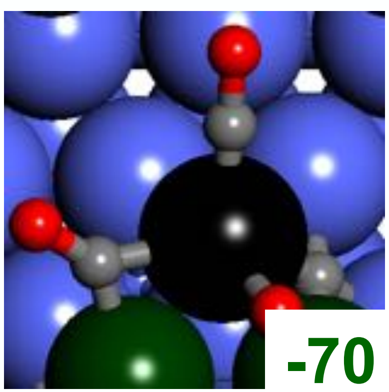


B5 corner

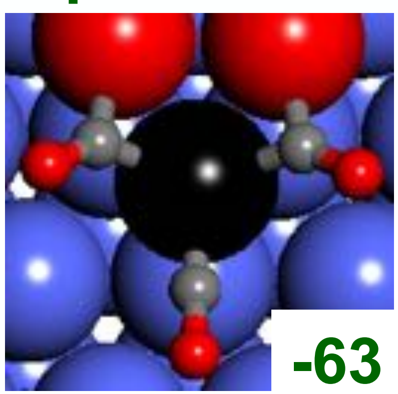


F4 corner

CO and C adsorption at corners



B5 corner



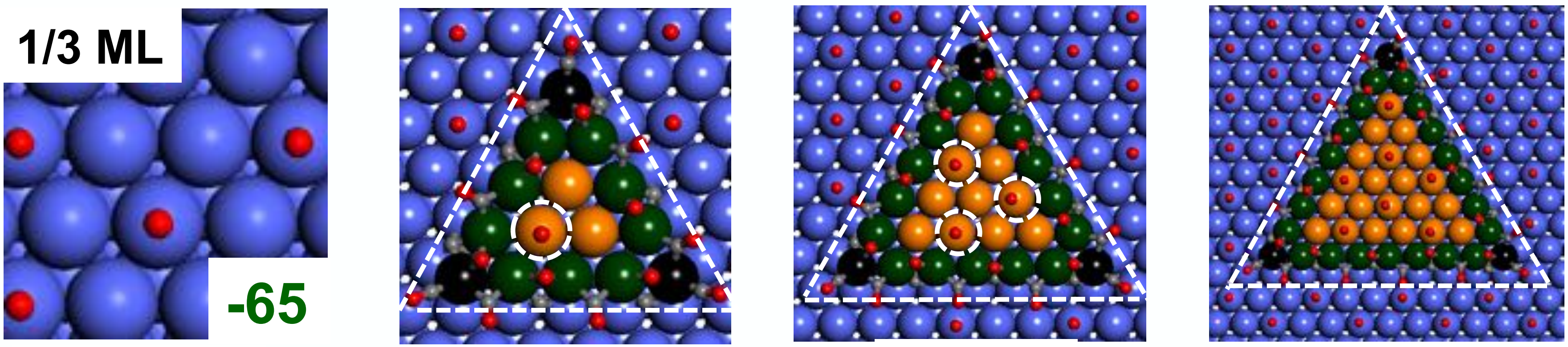
F4 corner

C adsorption at corner unfavorable
Stability at B5 ~ -20 kJ/mol

C coverage: 50% at corners;
CO coverage: 100% at corners

Creation of C/CO saturated B5 islands

CO adsorption free energy at island terraces?



Terraces Co_{15} Co_{28} Co_{45}

Energy balance for B5 island of 45 Co atoms:

Desorb CO from **66** terrace (indicated in white) sites: 66/3 x 65 = **+1430 kJ/mol**

Create **24** B5, 3 corners: 24 x 45 + 3 x 22 = **+1146 kJ/mol**

Adsorb CO on **21** island terrace sites: 21/3 x -65 = **-455 kJ/mol**

Adsorb 50%C/100%CO at **24** B5 sites: 9 x -18 + 18 x -88 = **-1746 kJ/mol**

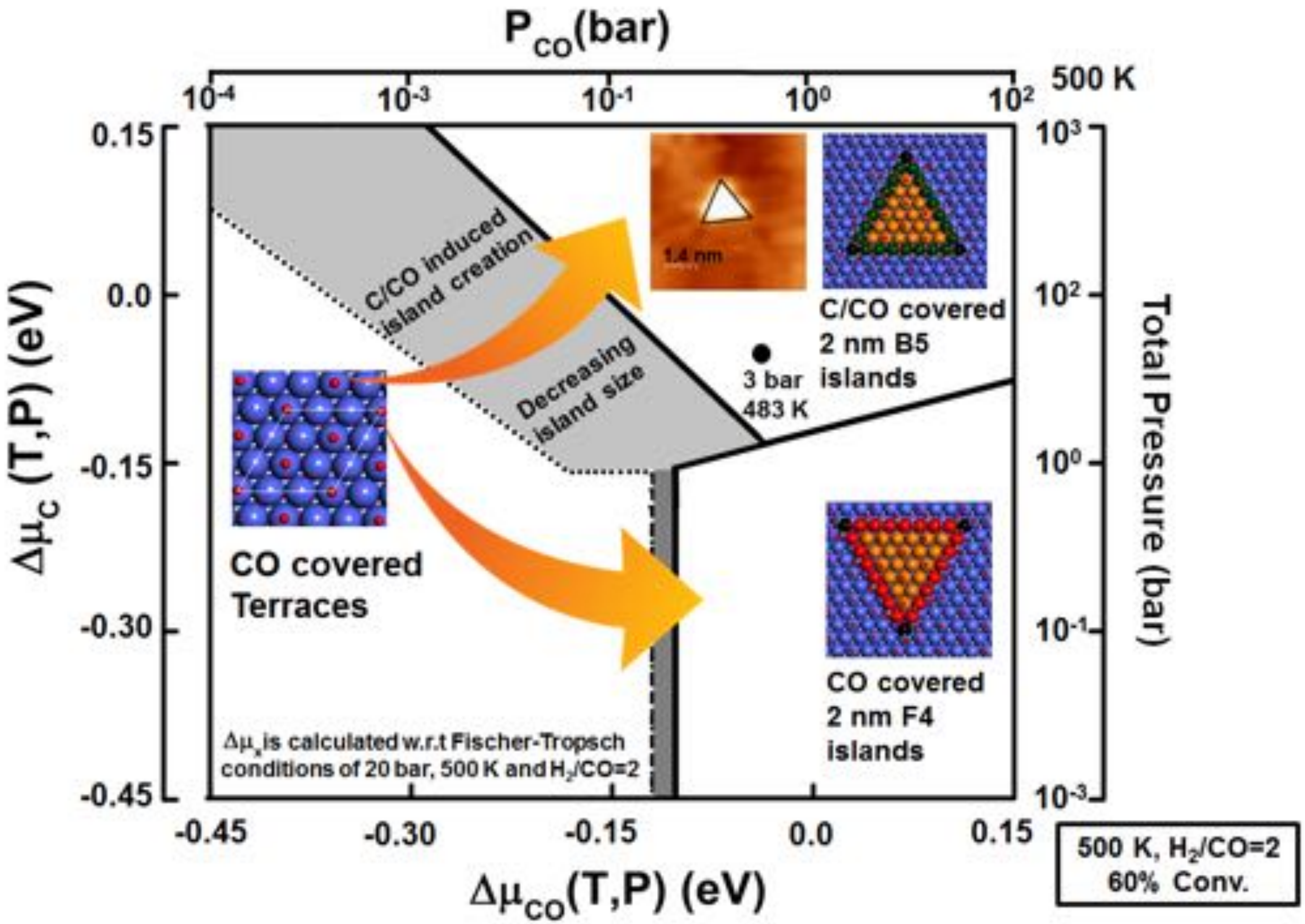
Adsorb C/CO at **3** corners: 3 x -14+ 9 x -70 = **-672 kJ/mol**

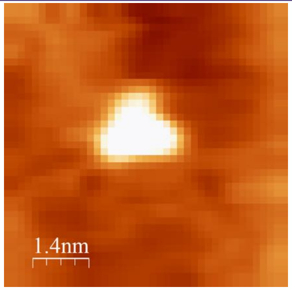
Overall: -297 kJ/mol islands or -6.6 kJ/mol Co atom for Co45

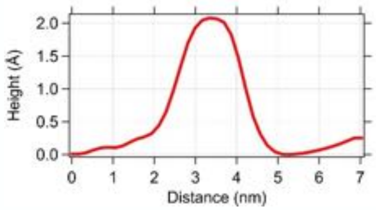
-393 kJ/mol islands or -5.9 kJ/mol Co atom for Co66

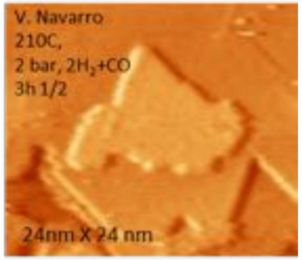
-126 kJ/mol islands or -4.5 kJ/mol Co atom for Co28

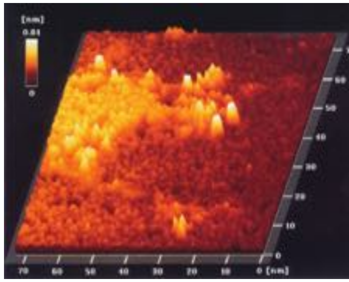
Effect of reaction conditions on Island stability







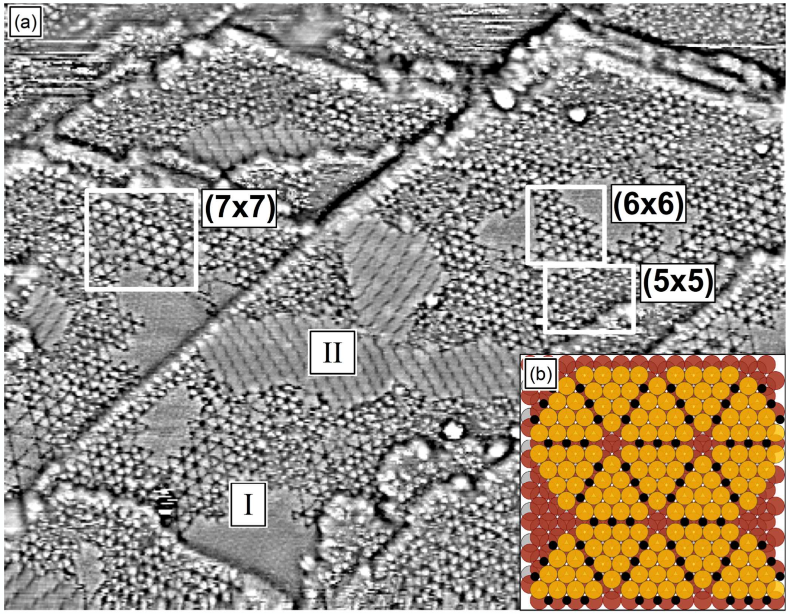


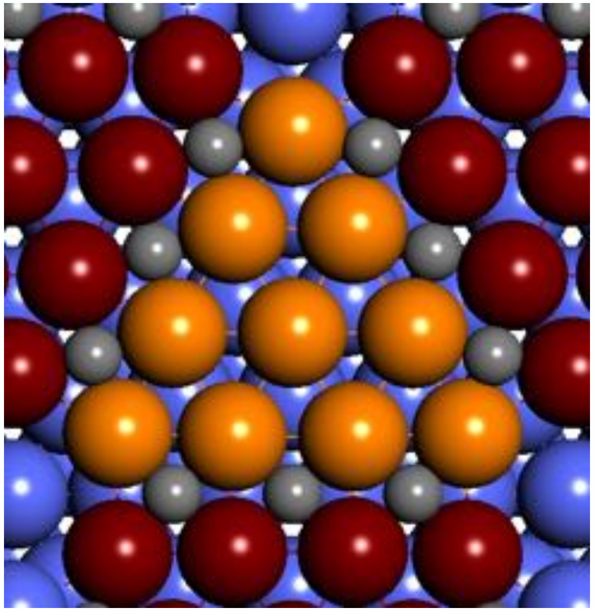


High CO, C chemical pot. drives Co_{45} island formation
Lower C chemical pot. --> lower C stability --> larger islands

* $\mu_{C/CO}$=0 at FT conditions (500 K, 20 bar, 60% conversion)

Islands observed by Joost Wintterlin





Ref: Wintterlin et al., *ACS Cat*, **2015**

Energy balance for island of 10 Co atoms:

Create **island** = **+260 kJ/mol**

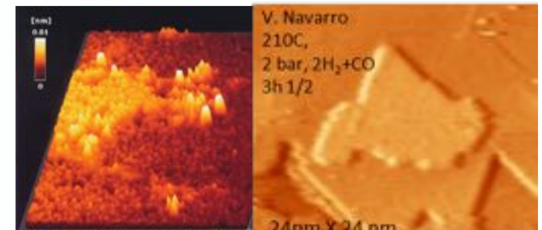
Cf. isolated Co10 = +472 kJ/mol

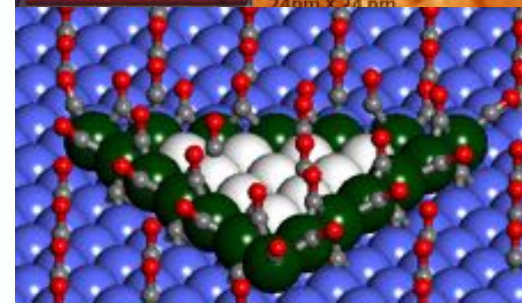
Adsorb C: 9/2 x **-48** = **-216 kJ/mol**

Cf. graphite: -69 kJ/mol

Total = +44 kJ/mol = +4.4 kJ/mol Co

CO de/adsorption – to do!





Structure: Reconstruction

Nature of experimentally observed islands

Origin of stability/formation

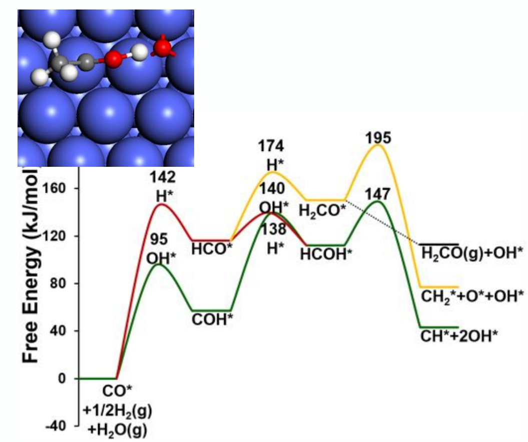
Refs: Banerjee *et al.*, *ACS. Catal.* **2015,** Banerjee *et al.*, **2016**

Activity: CO insertion and role OH

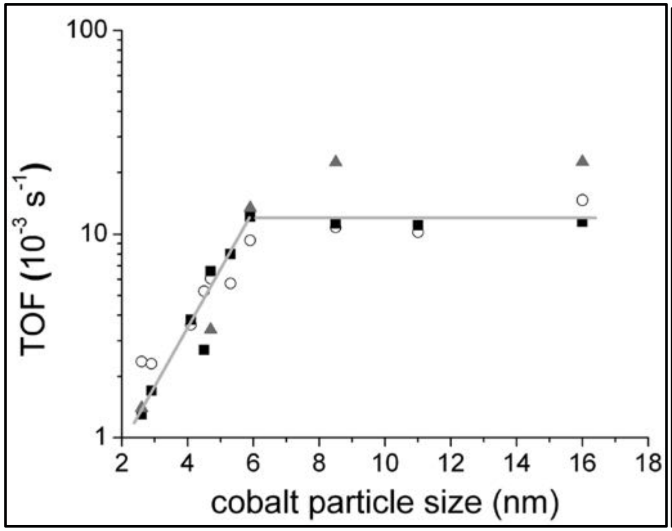
CO insertion consistent with kinetic data

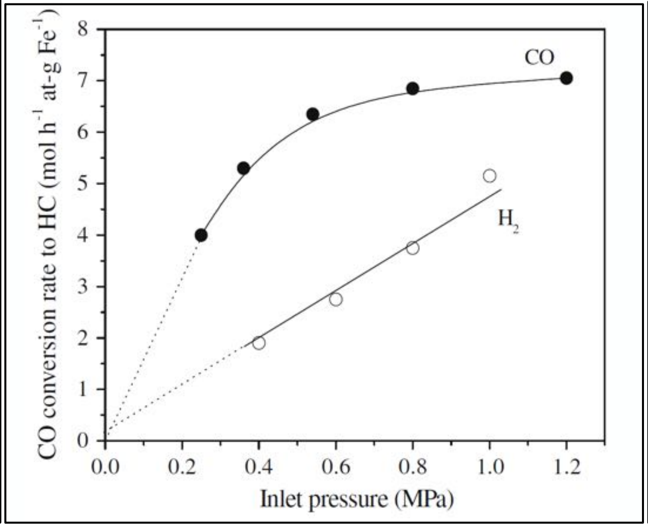
OH as hydrogenating species

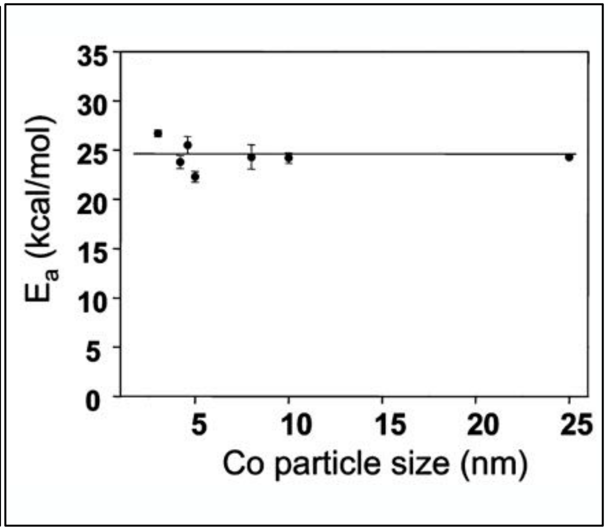
Refs: Zhuo *et al.*, *JPCC* **2009**, Zhou *et al.*, *J. Catal.* **2013**, Gunasooriya *et al.*, *Surf. Sci.* **2015,** Gunasooriya *et al.*, **2016**



Kinetic insights: Structure sensitivity, Order, E_a







TOF does not depend on particle size above 6 nm

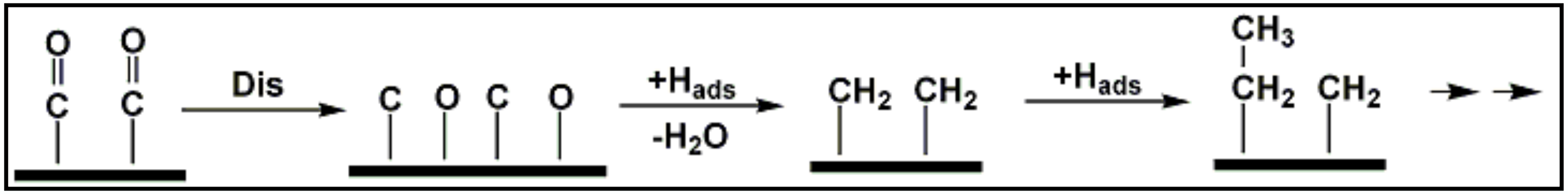
$$TOF = k_{surface}\,(K_{H2}\,p_{H2})^{1}\,(K_{CO}p_{CO})^{\sim 0} \sim 10^{-2}\,s^{-1}$$

$$E_{a,eff} = E_{surface} + \Delta H_{ads,H2} \qquad \Delta H_{ads,H2} \sim -50\ kJ/mol$$

$$E_{surface} \sim \underline{150\ kJ/mol}$$

de Jong *et al.*, *JACS* **2009**; Iglesia *et al.*, *J. Catal*. **2010**; Claeys *et al.*, *Stud. Surf. Sci. Cat.*, **1994**; Salmeron *et al.*, *JPCB* **2009**

Mechanistic proposals: Carbide mechanism



CH_x-CH_x coupling

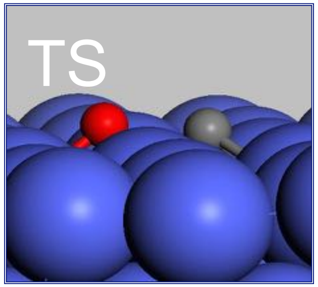
Brady-Pettit experiments with CH_2N_2: CH_x + CH_x coupling

C-C coupling on Co:

RCH + C → RCHC E_a = 71 kJ/mol

RCH + CH_2 → $RCHCH_2$ E_a = 68 kJ/mol

Need fast CO dissociation for **high CH_x coverage**



CO dissociation on Co(0001) terraces:

235 kJ/mol > 150 kJ/mol

CO dissociation slow → **low** C or CH_x **coverage**

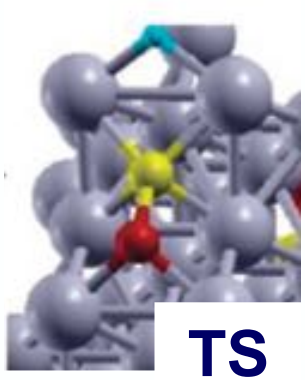
→**coupling slow compared to termination by hydrogenation**

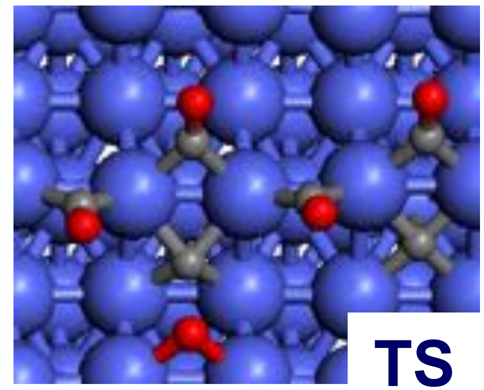
Brady, Pettit, *J. Am. Chem. Soc.*, **1980**; Lok *et al.*, *J. Catal.* **2008**

C-O activation at step defects

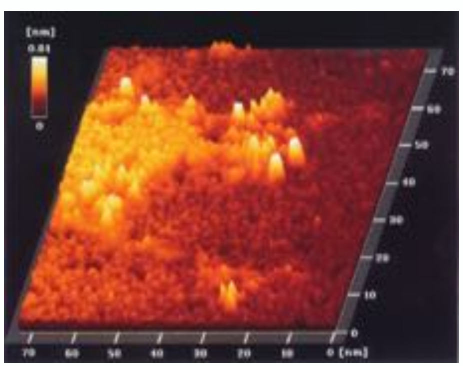
At special 6-fold step sites E_a = 70 kJ/mol

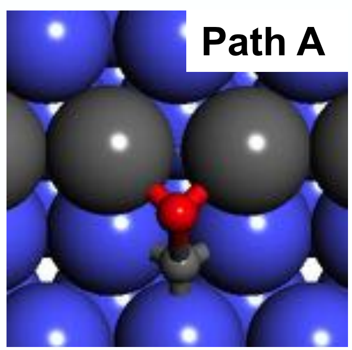
Are they present? Are they available?



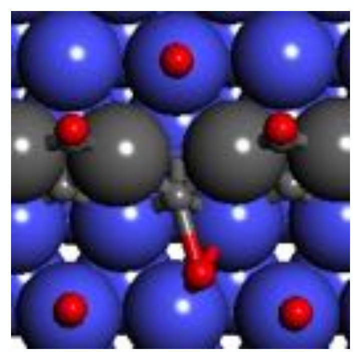


At Co_{45} nano-islands, B5 corners

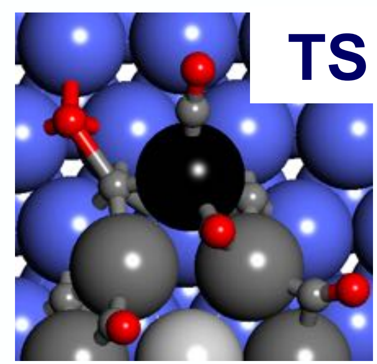




128 kJ/mol



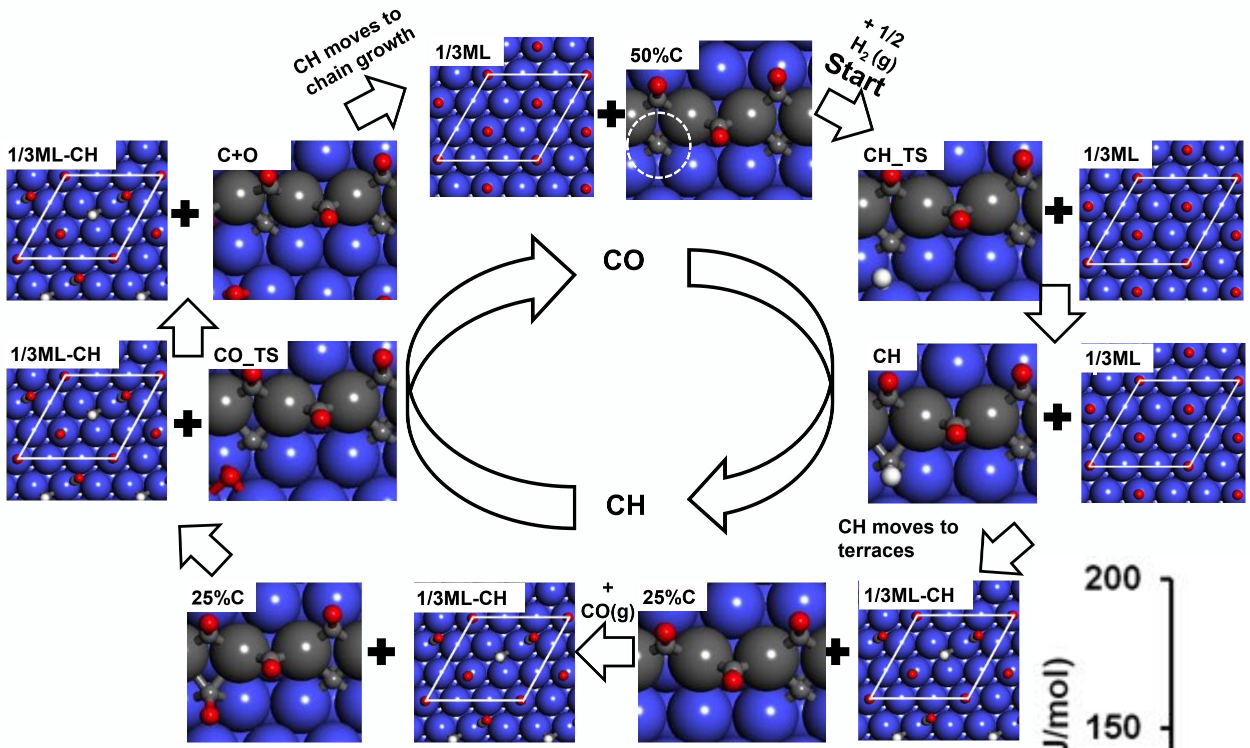
245 kJ/mol



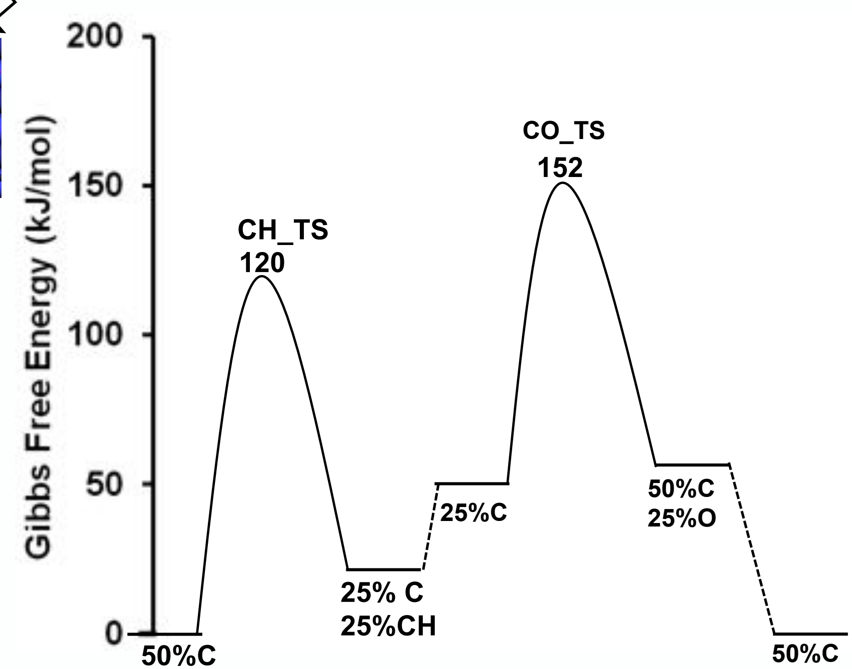
160 kJ/mol

van Santen *et al.*, *J. Am. Chem. Soc.*, **2009**; Saeys *et. al.*, *Angew. Chem.*, **2015**; Wilson, de Groot, *J. Phys. Chem.*, **1995**; Saeys *et al.*, *ACS Catal.* **2015**

C-O activation at C/CO covered step defects



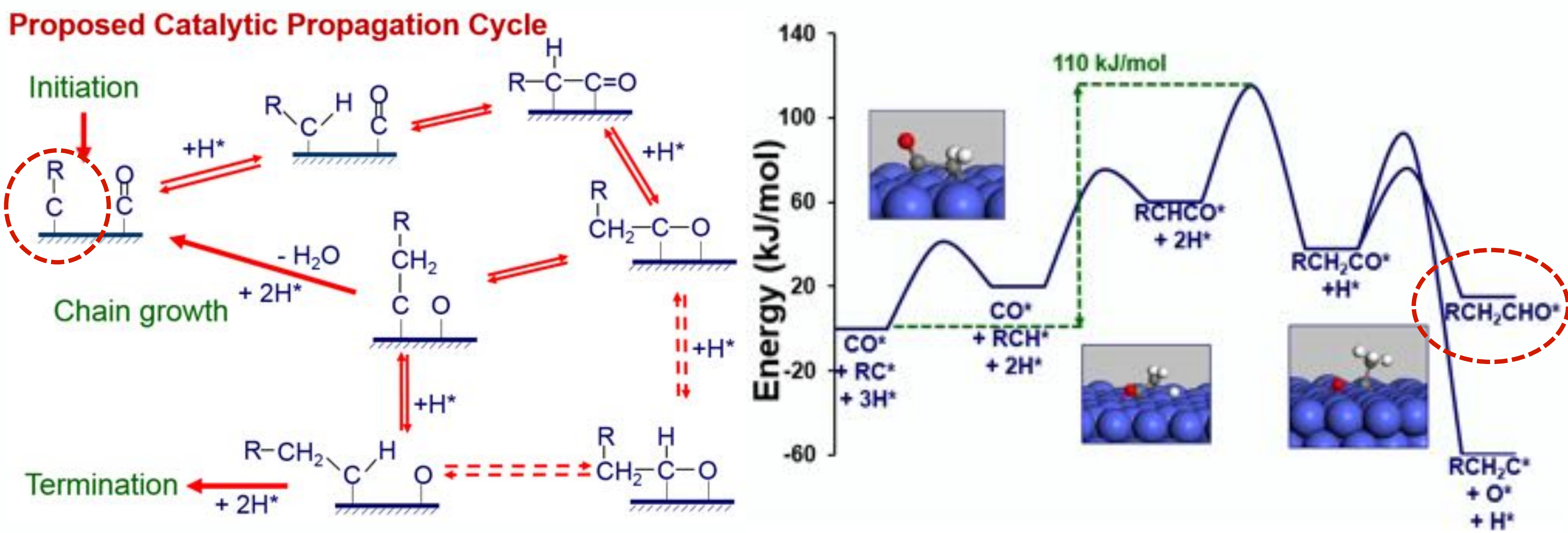
C_{B5} -> CH_{B5}
CH_{B5} -> $CH_{terrace}$
CO(g) -> CO_{B5}
CO_{B5} -> C_{B5}



Overall free energy barrier
~ 150 kJ/mol

TOF_{CO} ~ 1 10^{-3} s^{-1}

Mechanistic proposals: CO insertion mechanism



C-O activation after C-C bond formation

Proposed by Pichler and Schulz, 1970

RCH_2 + CO → **180 kJ/mol**, **but** RCH + CO much easier (60 kJ/mol)

Proposed cycle → **effective barrier 110 kJ/mol < 150 kJ/mol,** TOF ~ 0.01 s^{-1}

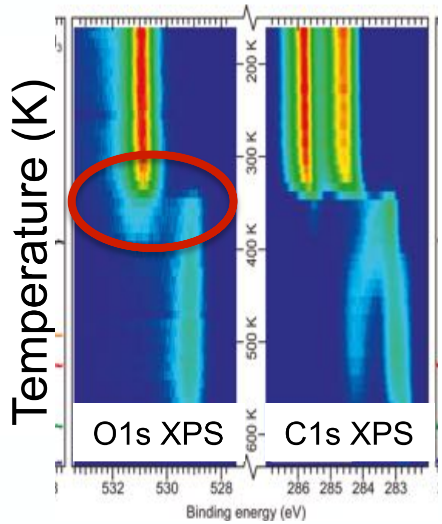
Need formation of **first CH**

Oxygenate selectivity – acetaldehyde formation

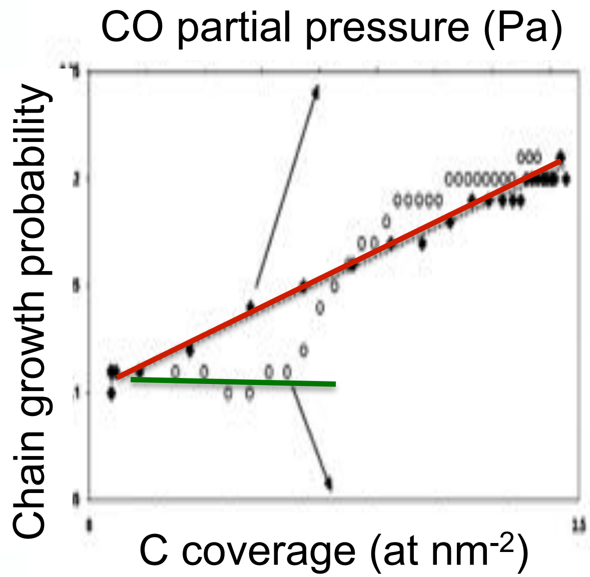
Pichler & Schulz, *Chem. Ing. Tech.*, **1970**; Saeys *et al.*, *J. Phys. Chem. C*, **2008** & *J. Catal.*, **2013**

Mechanistic proposals: CO insertion mechanism

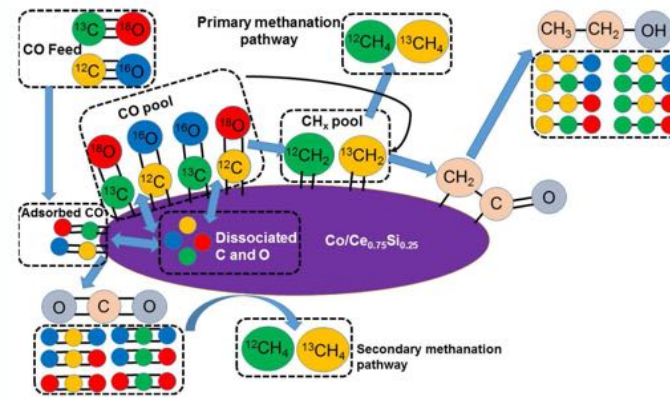
C-O scission[1] in RCH_x-O



Chain growth ~ CO



Isotope scrambling



Experimental support

Niemantsverdriet[1]: CH_3CH_x-O scission is fast

Kruse[2]: Chain growth ~ CO coverage, not C coverage

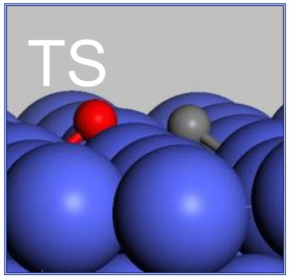
Davis[3]: ^{13}C-^{18}O isotope labelling -> CO insertion

1. Niemantsverdriet *et al.*, *JPC Lett.* **2010**; 2. Schweicher, Bundhoo, Kruse, *JACS* **2012**;
3. Davis *et al.*, *Ind. Eng. Chem. Res.*, **2015**

C-O activation – still required

Direct C-O dissociation

$CO^* \rightarrow C^* + O^*$ 235 kJ/mol at low CO coverage,
254 kJ/mol at 1/3 ML CO coverage



H-assisted C-O dissociation

Hydrogenation

$CO^* + H^* \rightarrow HCO^*$ or COH^*

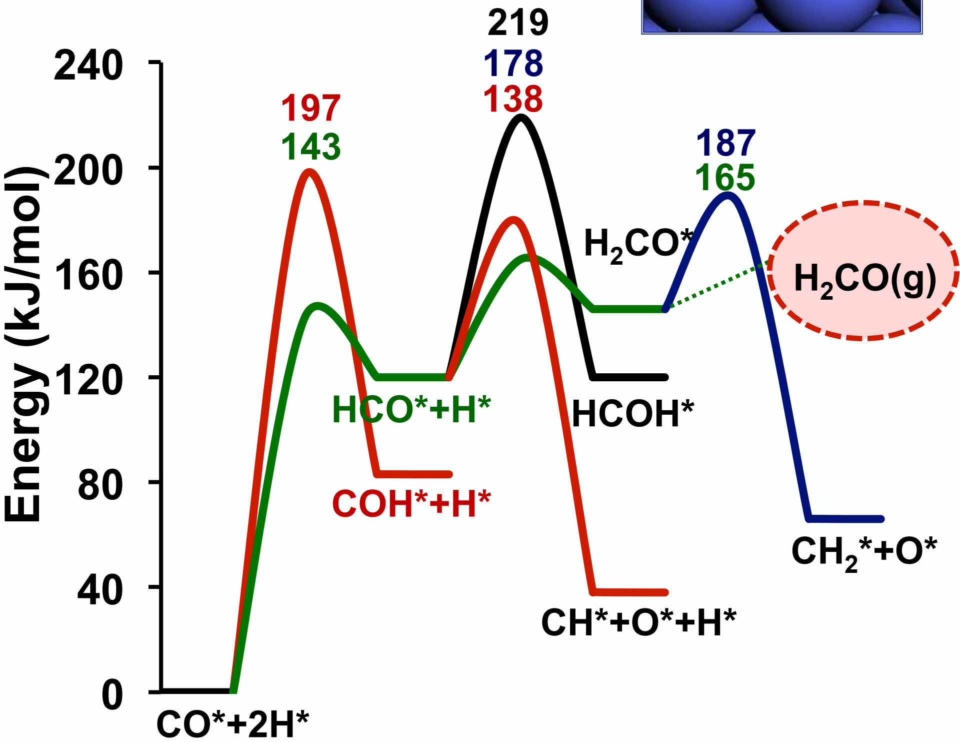
$HCO^* + H^* \rightarrow H_2CO^*$ or $HCOH^*$

C-O scissions

$HCO^* \rightarrow HC^* + O^*$

$H_2CO^* \rightarrow CH_2^* + O^*$ or $CH_2O(g)$

$HCOH^* \rightarrow HC^* + OH^*$

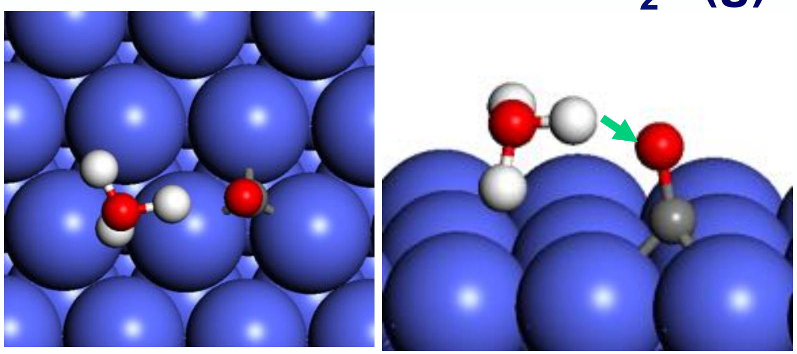


High effective barriers, $CH_2O(g)$ formaldehyde formation

Could water facilitate CO activation?

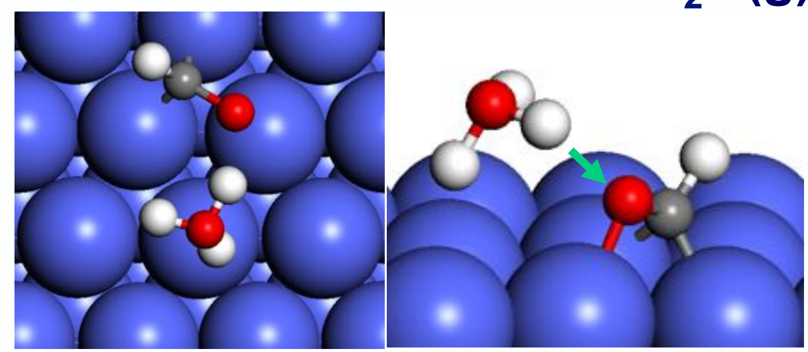
Proton shuttling pathway

$CO^* + \frac{1}{2} H_2(g) + H_2O(g) \rightarrow$ $COH^* + H_2O(g)$



E_a = 82 kJ/mol

$HCO^* + \frac{1}{2} H_2(g) + H_2O(g) \rightarrow$ $HCOH^* + H_2O(g)$



E_a = 63 kJ/mol

Direct mechanism

Reactants	Products	E_a (kJ/mol)
$CO^* + \frac{1}{2} H_2(g)$	COH^*	166
	HCO^*	112
$HCO^* + \frac{1}{2} H_2(g)$	$HCOH^*$	68
	H_2CO^*	16

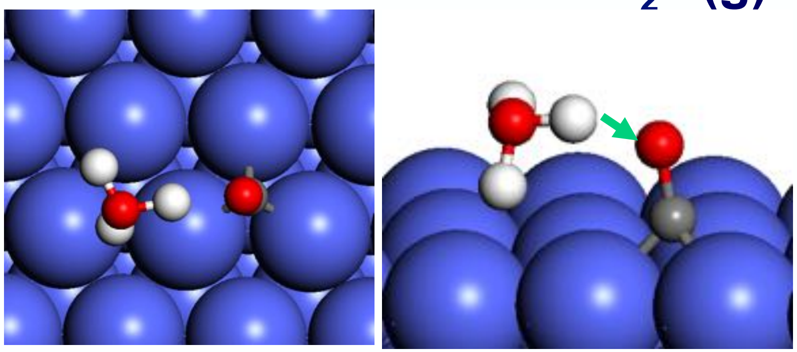
Low energy barrier to form COH^*, $HCOH^*$ via proton shuttling

Iglesia *et al.*, *Angew. Chem.*, **2013**

Could water facilitate CO activation?

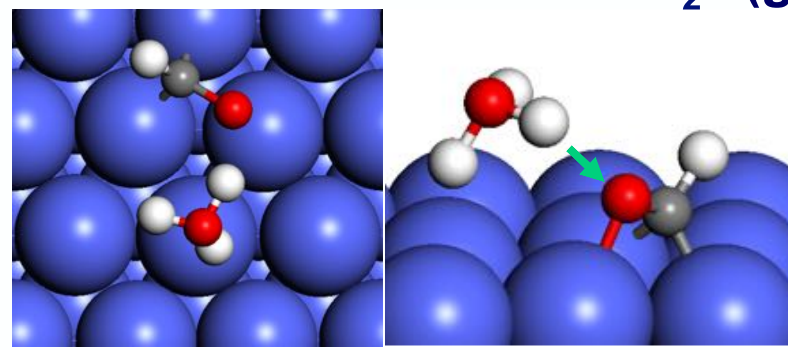
Proton shuttling pathway

$CO^* + \frac{1}{2} H_2(g) + \underline{H_2O(g)} \rightarrow$ $COH^* + H_2O(g)$



ΔG_a = 153 kJ/mol

$HCO^* + \frac{1}{2} H_2(g) + \underline{H_2O(g)} \rightarrow$ $HCOH^* + H_2O(g)$



ΔG_a = 167 kJ/mol

Direct mechanism

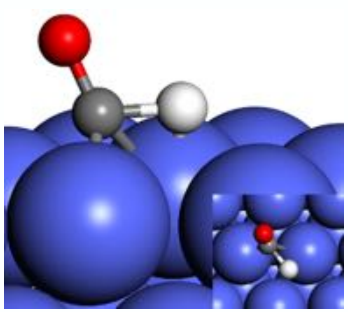
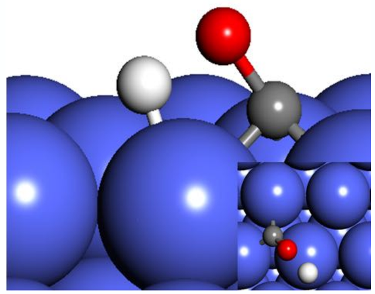
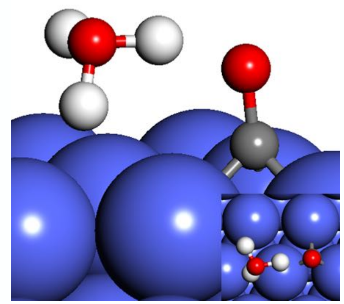
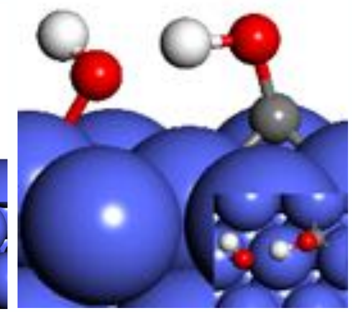
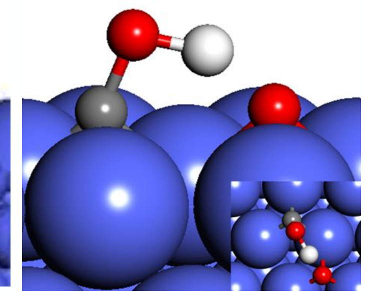
		ΔG_a (kJ/mol)
$CO^* + \frac{1}{2} H_2(g)$	→ COH^*	189
	→ HCO^*	137
$HCO^* + \frac{1}{2} H_2(g)$	→ $HCOH^*$	88
	→ H_2CO^*	40

Formation of $(CO\text{-}H\text{-}H_2O)^{**}$ cost a significant entropy penalty.

"Direct" hydrogenation to HCO remains dominant.

H_2O^*/OH^* as hydrogenating species?

HCO* formation | **COH* formation**

	CO^*+H^*	CO^*+H^*	$CO^*+H_3O^*$	$CO^*+H_2O^*$	CO^*+OH^*
					
E_a	143	197	82	70	96
ΔG_a	137	189	153	139	94

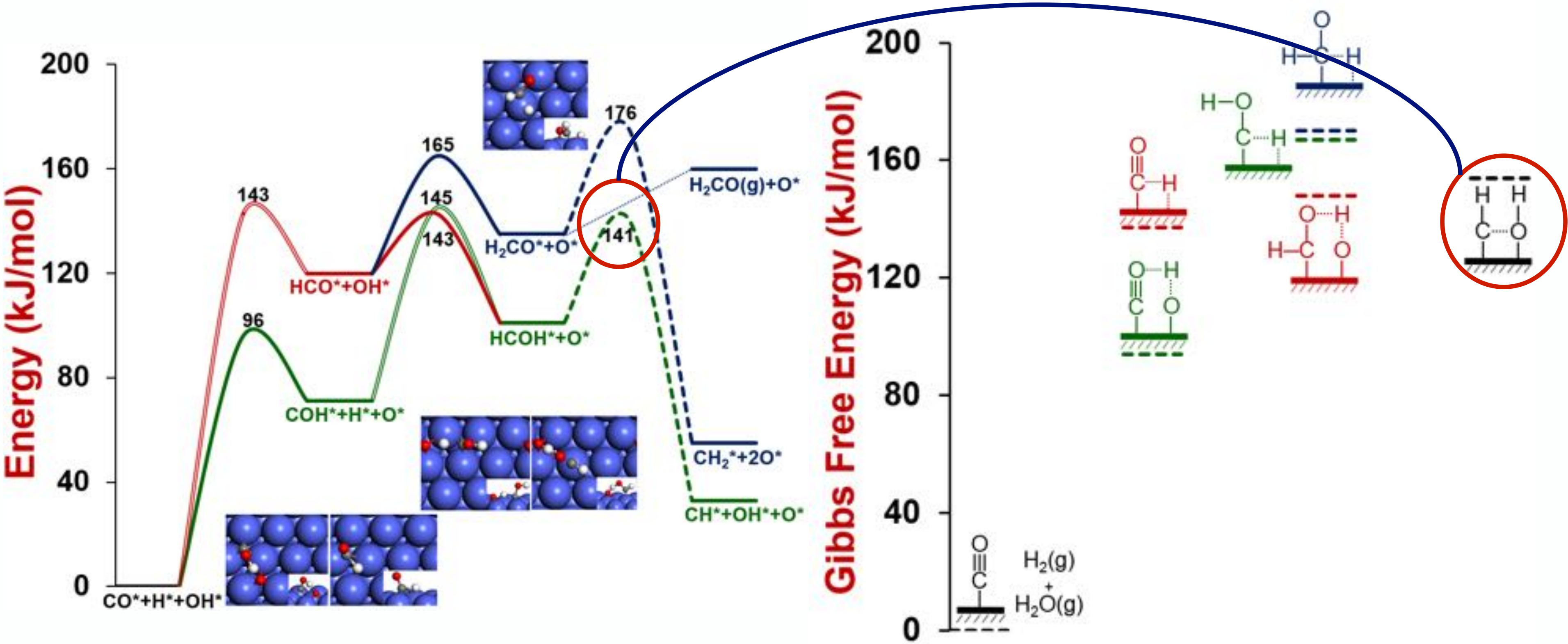
Note: Effective ΔG_a is relative to $CO^* + ½\ H_2(g) + \underline{H_2O(g)}$

OH* favors O-atom hydrogenation while surface H* favors C-atom hydrogenation

OH* coverage?	$\Delta G_{forward,rxn}$
$H_2O(g) + * \rightarrow OH^* + ½\ H_2(g)$	-6

Significant thermodynamic OH* coverage during FT

OH* as hydrogenating species?



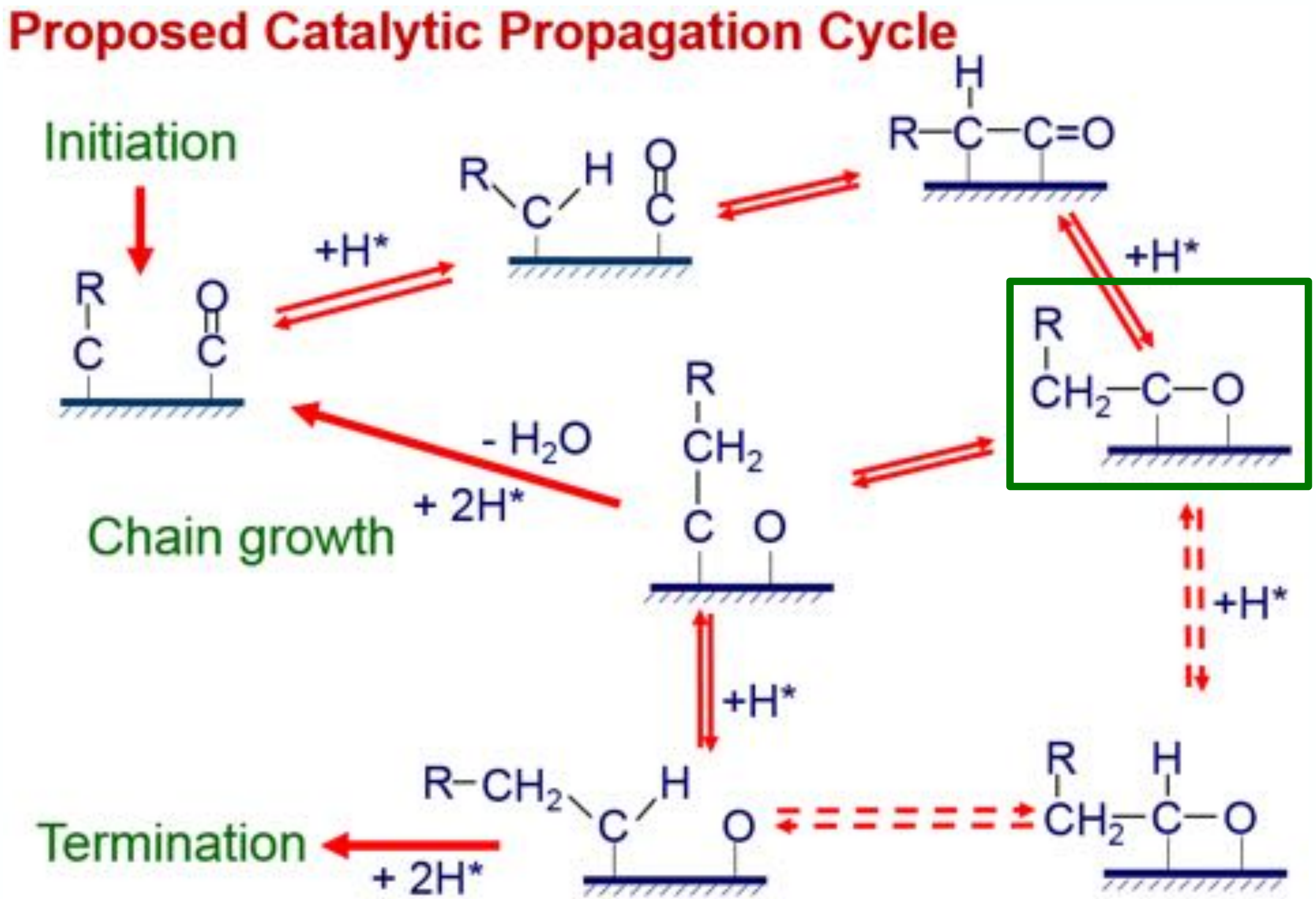
HCOH formation favored over H_2CO formation

CH-OH dissociation rate limiting

Effective barrier ~150 kJ/mol

TOF = kT/h exp $(-\Delta G_a/RT)\ \theta_{CO^*}\ p_{H2O(g)}$ **~ 5 x10^{-3} s^{-1}**

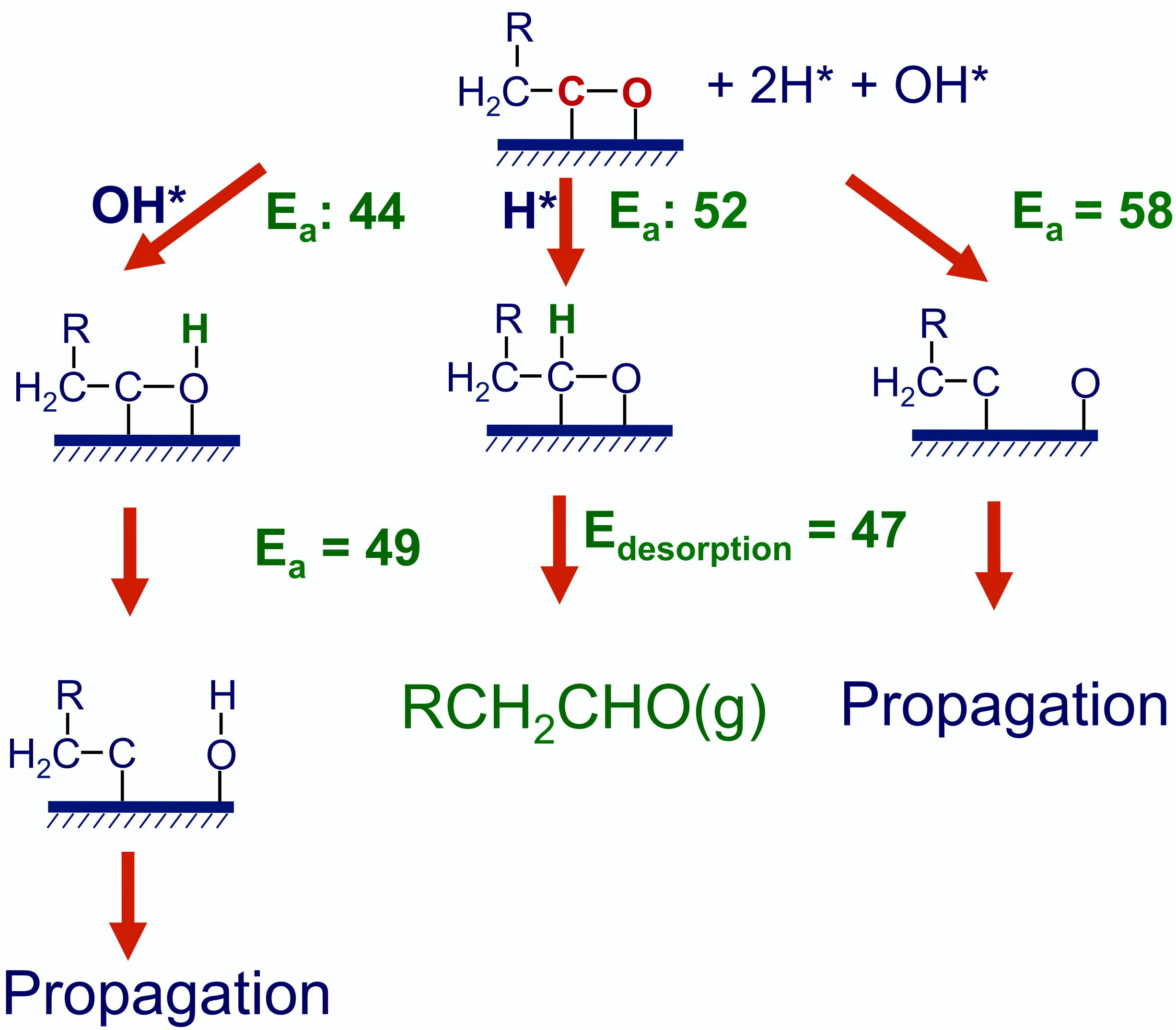
Mechanistic proposals: CO insertion mechanism



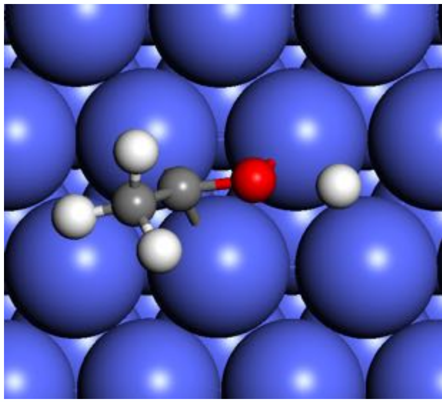
RCH$_2$CO* key intermediate: Determines selectivity

Saeys *et al.*, *J. Phys. Chem. C*, **2008** & *J. Catal.*, **2013**

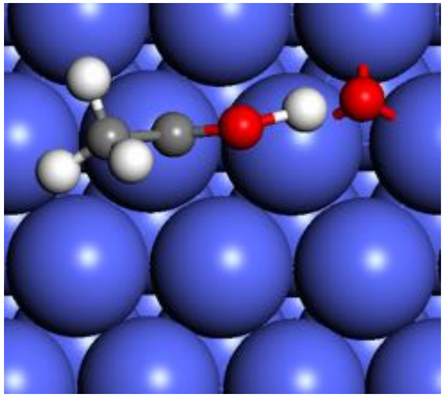
CO insertion mechanism: RCO* Pathways



CH_3COH^* formation



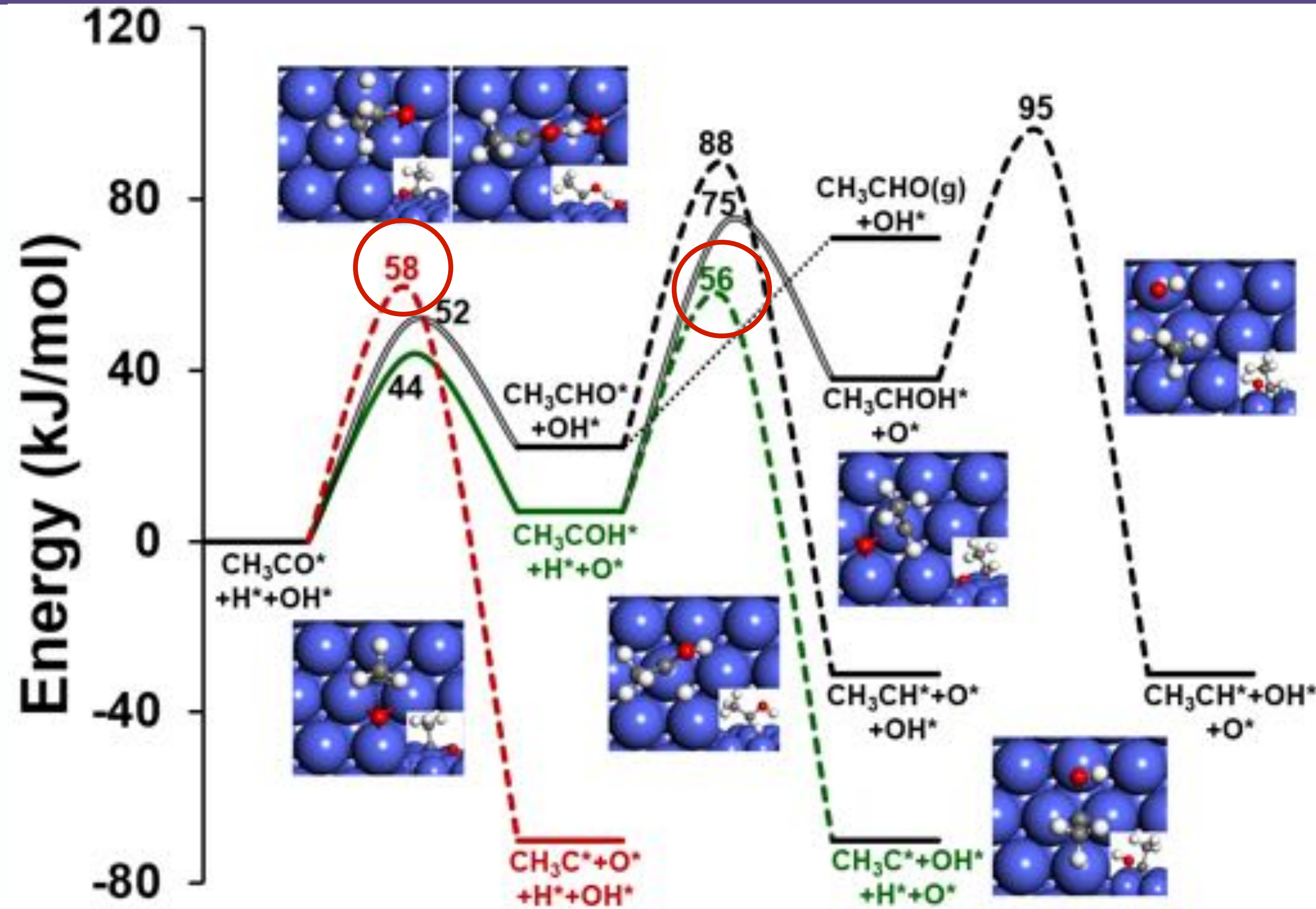
E_a: 196 kJ/mol



E_a: 44 kJ/mol

RCH_2CO^* key intermediate: Determines selectivity

CO insertion mechanism: RCO* Pathways

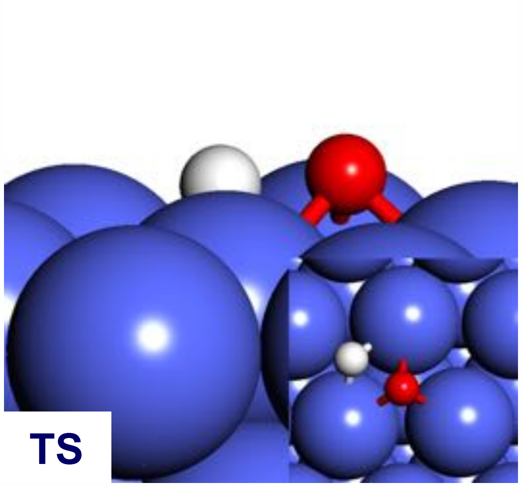


In the presence of OH*, a new pathway to form RCH_2C via RCH_2COH opens up.

No obvious dominant pathway, detailed microkinetic model

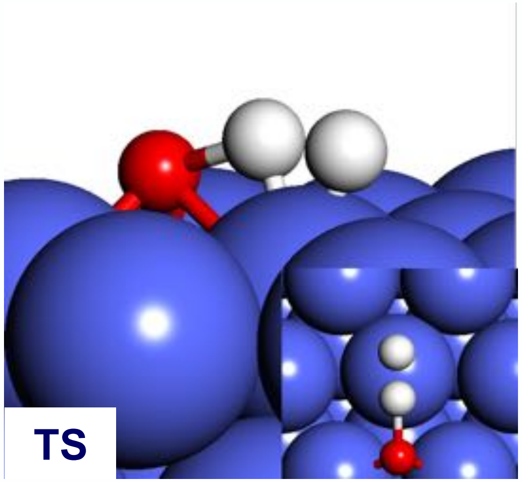
What happens to O*?

$O^* + H^* \rightarrow OH^* + *$



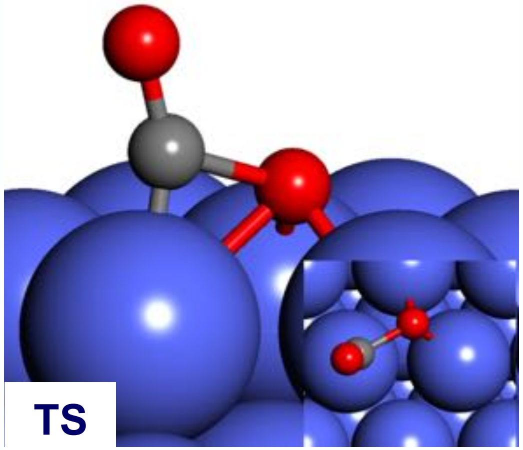
E_a: 121 kJ/mol
ΔG_a: 115 kJ/mol
Exp[1]: 129 +/- 7 kJ/mol

$O^* + H_2(g) + * \rightarrow H^* + OH^*$



E_a: 69 kJ/mol
ΔG_a: 110 kJ/mol

$O^* + CO^* \rightarrow CO_2 + *$



E_a: 138 kJ/mol
ΔG_a: 136 kJ/mol
Higher barrier

Heterolytic H_2(g) adsorption on O* regenerates OH*

$$TOF = kT/h \exp(-\Delta G_f/RT)\, \theta_{O^*} p_{H2(g)} \sim 1600\ s^{-1}$$

Higher barrier for CO_2 formation

Weststrate *et al.*, *JPCC*, **2016**

Conclusions

Reconstruction of Co terraces driven by synergistic adsorption of σ-aromatic sq pl C and CO at B5 sites

Balance between edge and corner stability leads to triangular, 2 nm islands under FT conditions, but depends on equilibrium

CO insertion mechanism via RCH + CO is a viable mechanism on CO-covered Co terraces

OH* groups are a source of hydrogens (protons) under FT conditions and open a new hydrogenation pathway

Students: Arghya Banerjee (NUS), Kasun Gunasooriya (UGent)
Collaborators: Herman Kuipers and Sander van Bavel (Shell)
Funding: Shell Global Solutions, Odysseus-Flemish Research Foundation